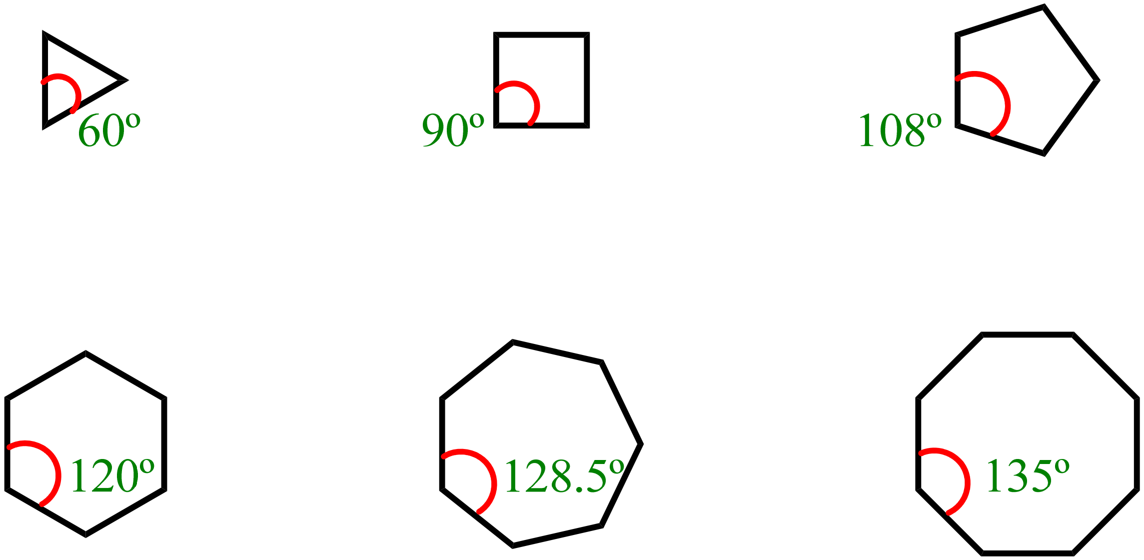
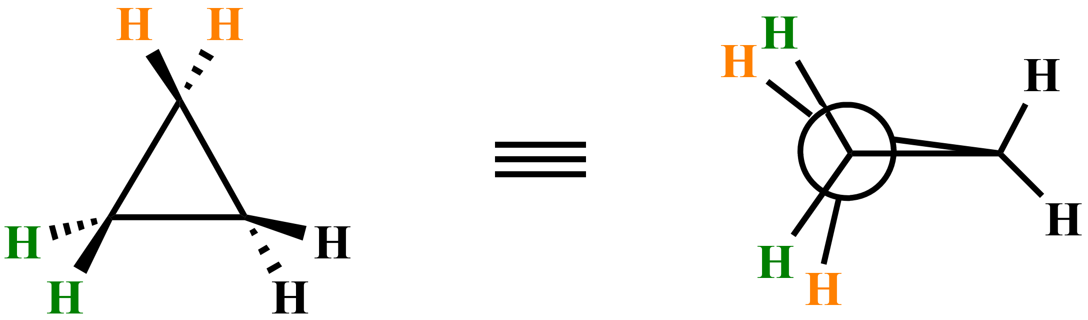
# Conformations of Cycloalkanes

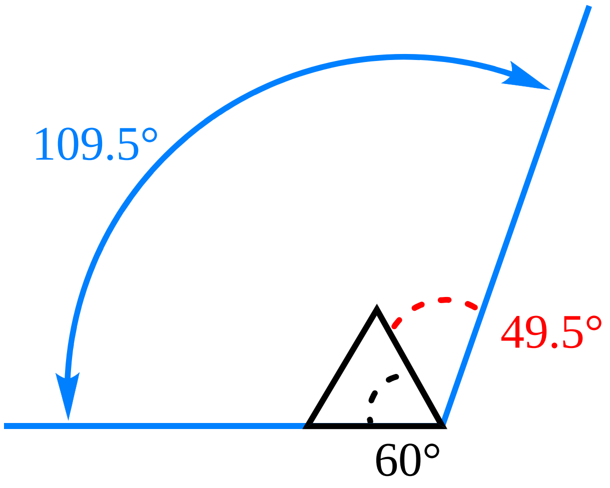


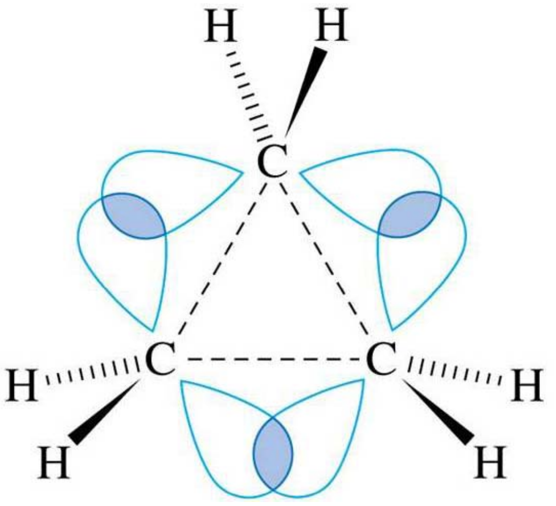
Cycloalkanes are not always planar structures. Being planar requires large variations in bond angles from the ideal value of 109.5º for a tetrahedral carbon.

# Cyclopropane



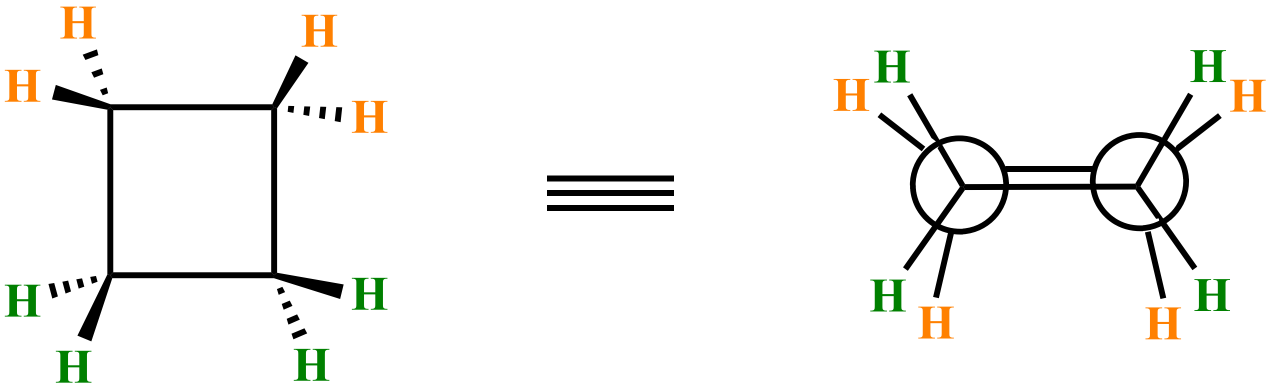
Cyclopropane has a high degree of torsional strain due to large number of eclipsing interactions.



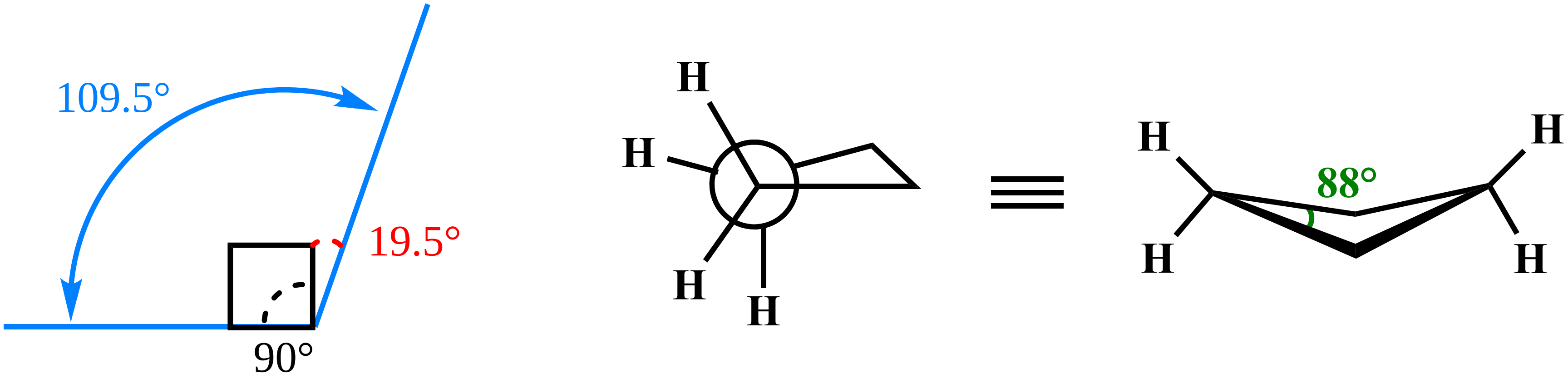


The large angular strain in cyclopropane is compensated partially through ***bent bonds***

# Cyclobutane



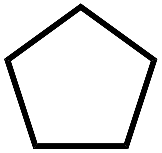
Cyclobutane has eight H---H eclipsing interactions in a planar structure

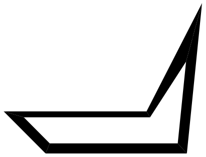


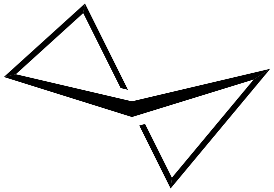
Torsional strain in cyclobutane is reduced by adopting a slightly folded structure, which results in additional angular strain

# Cyclopentane

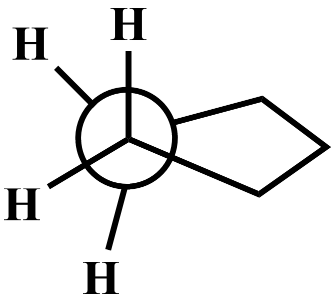
A planar structure for cyclopentane would have bond angles of 108°, which is very close to the ideal values for a tetrahedral carbon atom. However, such a structure could lead to considerable torsional strain resulting from ten H---H eclipsing interactions.


Planar
All C-atoms in one plane


Envelope
Four C-atoms in one plane

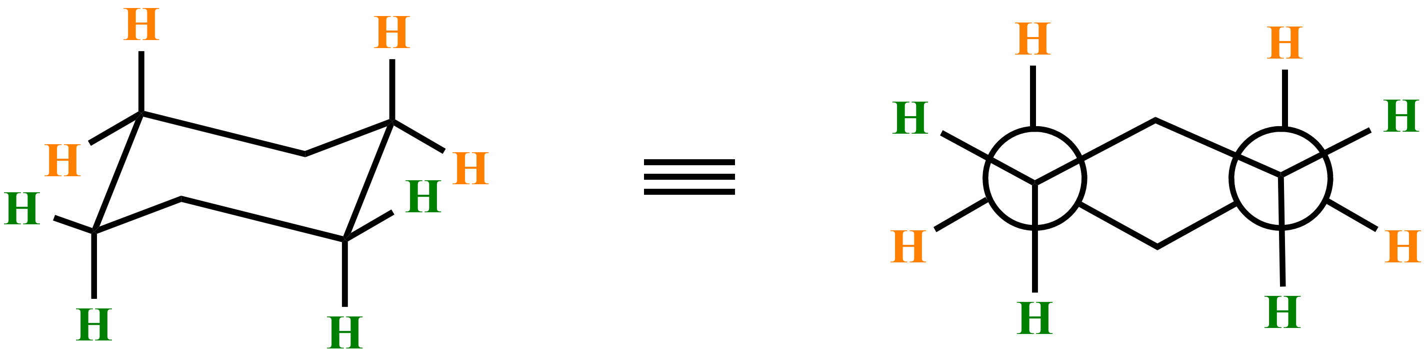

Half-chair
Three C-atoms in one plane

Torsional strain is reduced by moving one or two carbon away from the plane. This results in an increase in angular strain. Carbon atoms move in and out of the plane rapidly, resulting in an illusion of rotation of the molecule. This phenomenon is termed as **pseudo-rotation**.

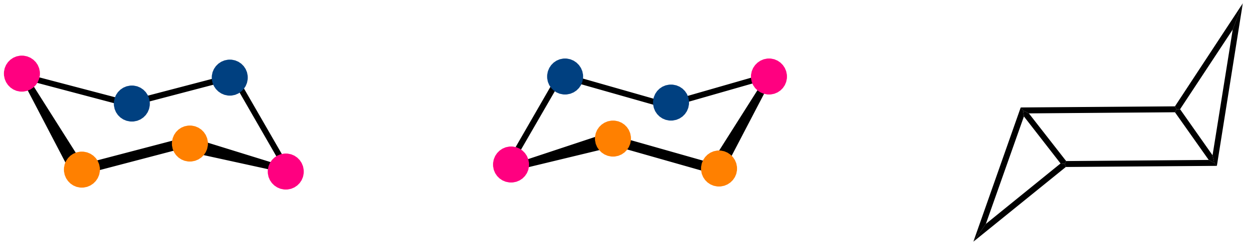


# Cyclohexane

Cyclohexane avoids torsional interactions by adopting non-planar conformations, which also reduces the bond angles to that of a perfect tetrahedron (~109.5°).



The **chair conformation** of cyclohexane is the most stable. It has no torsional strain as all the C-H bonds are staggered to each other. The bond angle is very close to the ideal value.

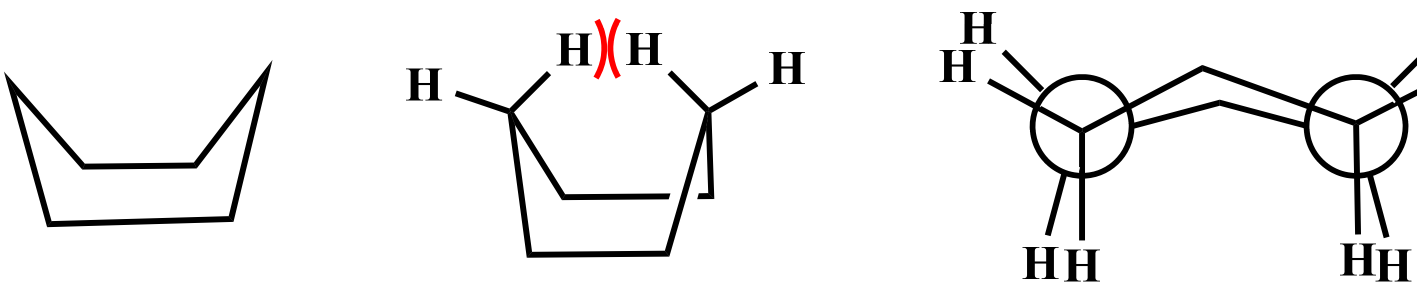


The chair conformation can be viewed as having two carbon atoms on the plane of the paper. Two in another plane in front of the paper and the remaining two in a third plane, behind the plane of the paper

# Cyclohexane

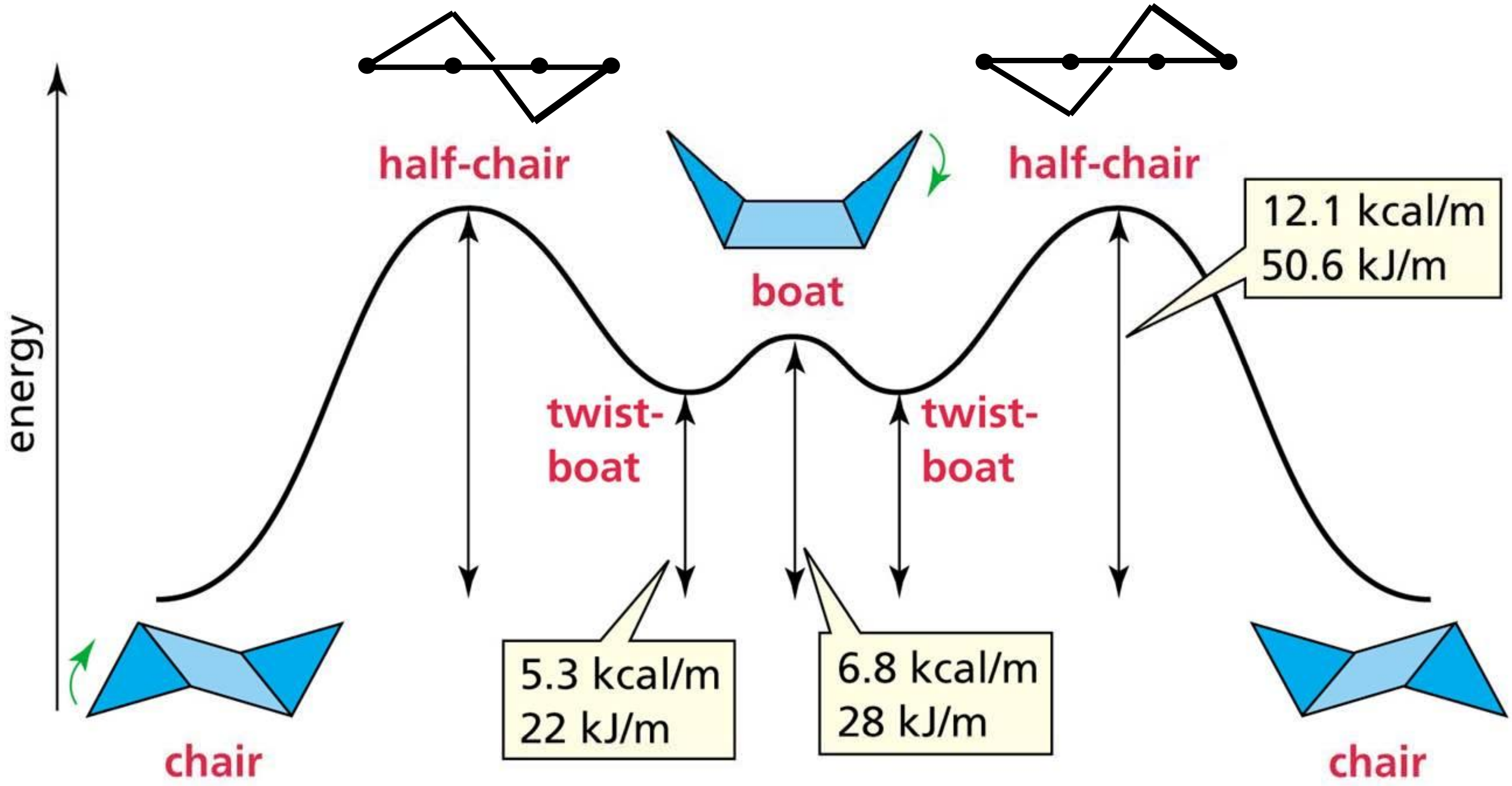
Cyclohexane forms a number of different conformers. However, structures other than the chair conformation suffers from torsional strain, angular strain or both.

**Boat Conformation:** It has no angular strain. However, in addition to the torsional strain resulting from 4 H---H interactions, it also has a flagpole interaction between the hydrogen atoms on 1- and 4-carbon atoms.



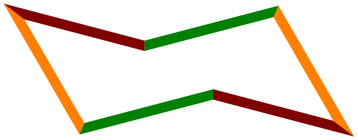
**Twist Conformation:** It is more stable than the boat conformation, but less stable than the chair conformation. The flagpole interactions and torsional strain in the boat conformation are reduced in the twist conformer.

# Conformational Analysis of Cyclohexane

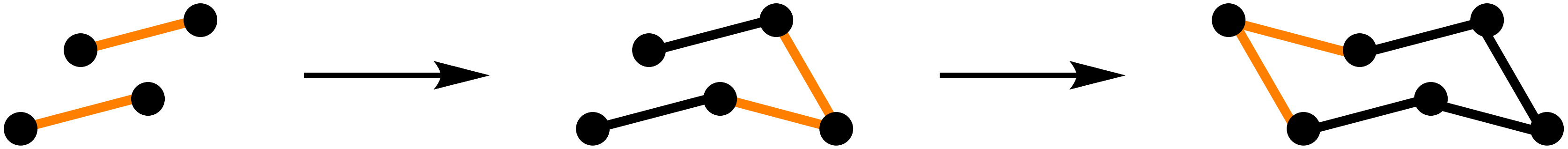


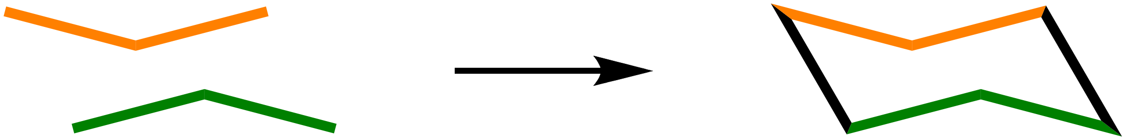
The cyclohexane continuously flips from one chair conformation to the other. Approximately 1 million such interconversions occur every second. More than 99% of the molecules are estimated to be in a chair conformation at any given time.

# Drawing the Chair Conformation of Cyclohexane



Opposite bonds are drawn parallel to each other.

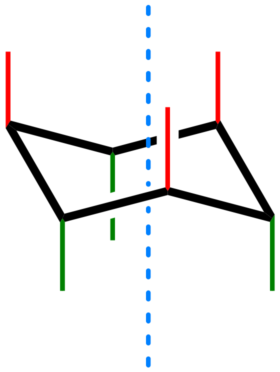




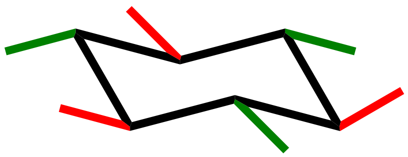
# Axial and Equatorial Bonds

**Axial Bonds:** They are parallel to each other and to the principal axis, but perpendicular to the average plane of the ring. There are three bonds facing up and three facing down.

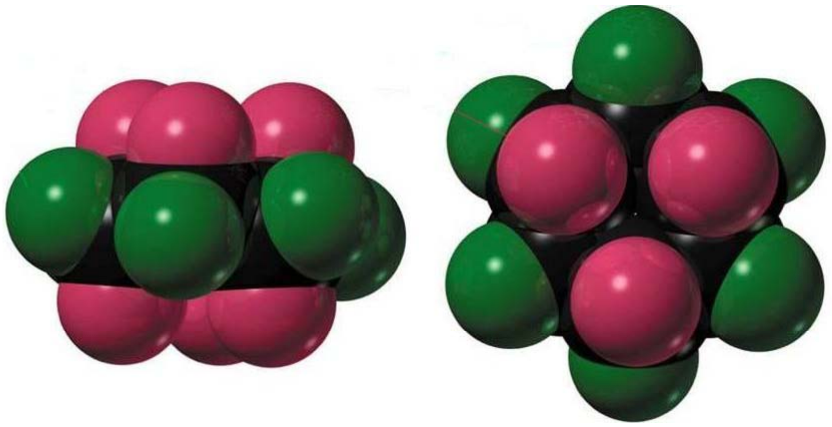
**Equatorial Bonds:** These are three sets of two parallel bonds, each of which are parallel to two of the bonds in the ring. Equatorial bonds alternate from slightly up to slightly down orientation on moving from one carbon to the next



Axial Bonds



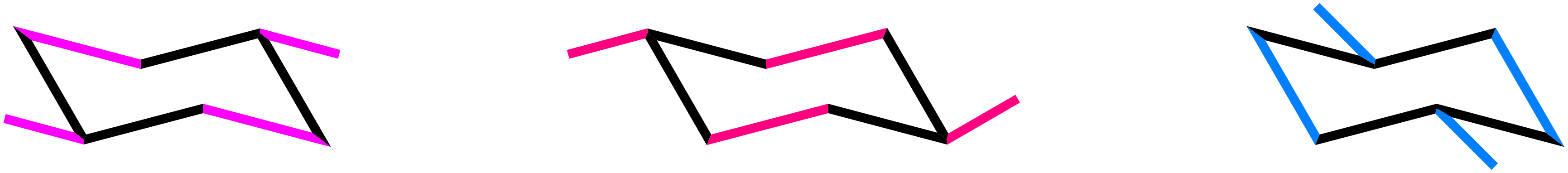
Equatorial Bonds



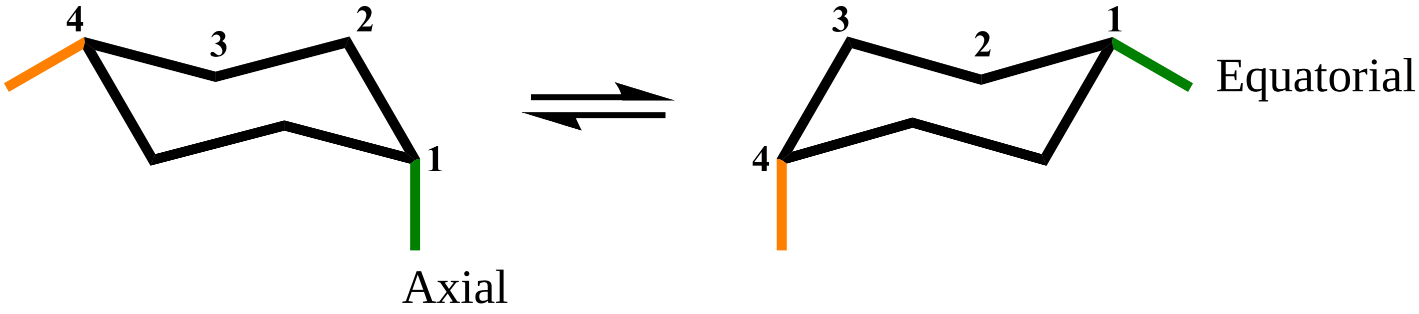
Axial (red) and equatorial (green) bonds as viewed from the side (L) and top (R).

# Axial and Equatorial Bonds

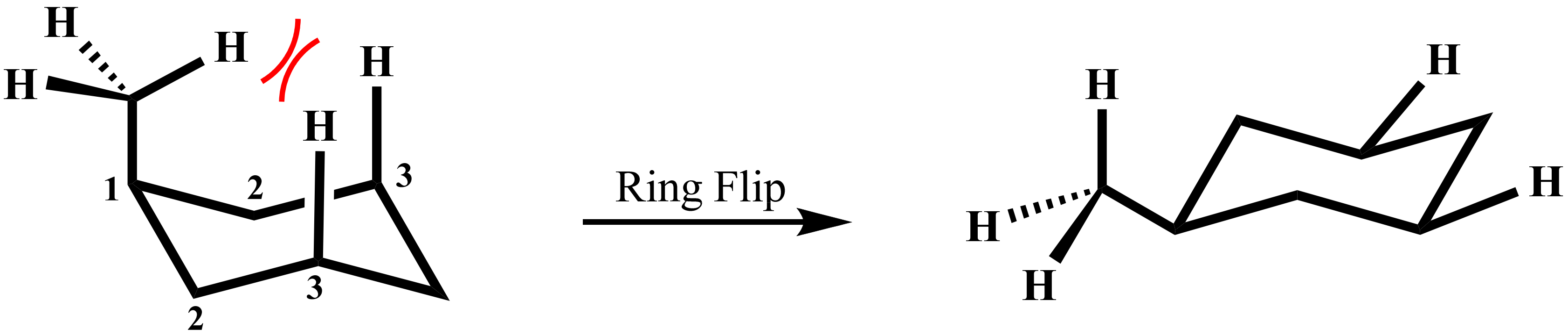
Each equatorial bond is parallel to two carbon-carbon bonds in the ring and another equatorial bond.



Axial and equatorial bonds undergo interconversion, when a chair conformation flips to the other. However, their relative orientations in space do not change.

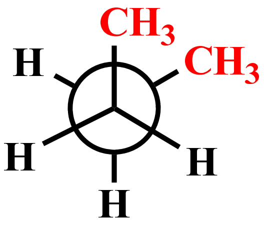


# Mono-substituted Cyclohexane

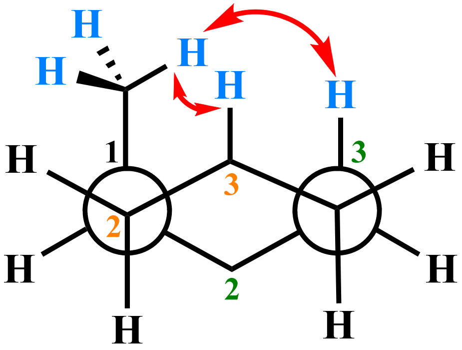


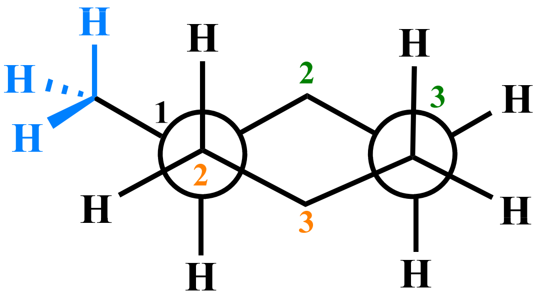
Any substitution bigger than hydrogen in an axial position leads to unfavorable interactions with axial hydrogen atoms on the 3-carbon atom. Such an interaction is generally termed as **1,3-diaxial interaction**.

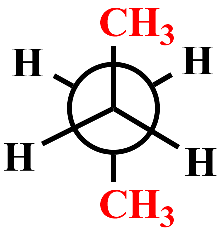
In the case of a methyl substituent, these interactions are exactly same as a gauche butane interaction and amounts to 1.8 kcal/mol (two such interactions). In an equatorial position, the methyl group is anti to C3 in the ring.



*gauche*

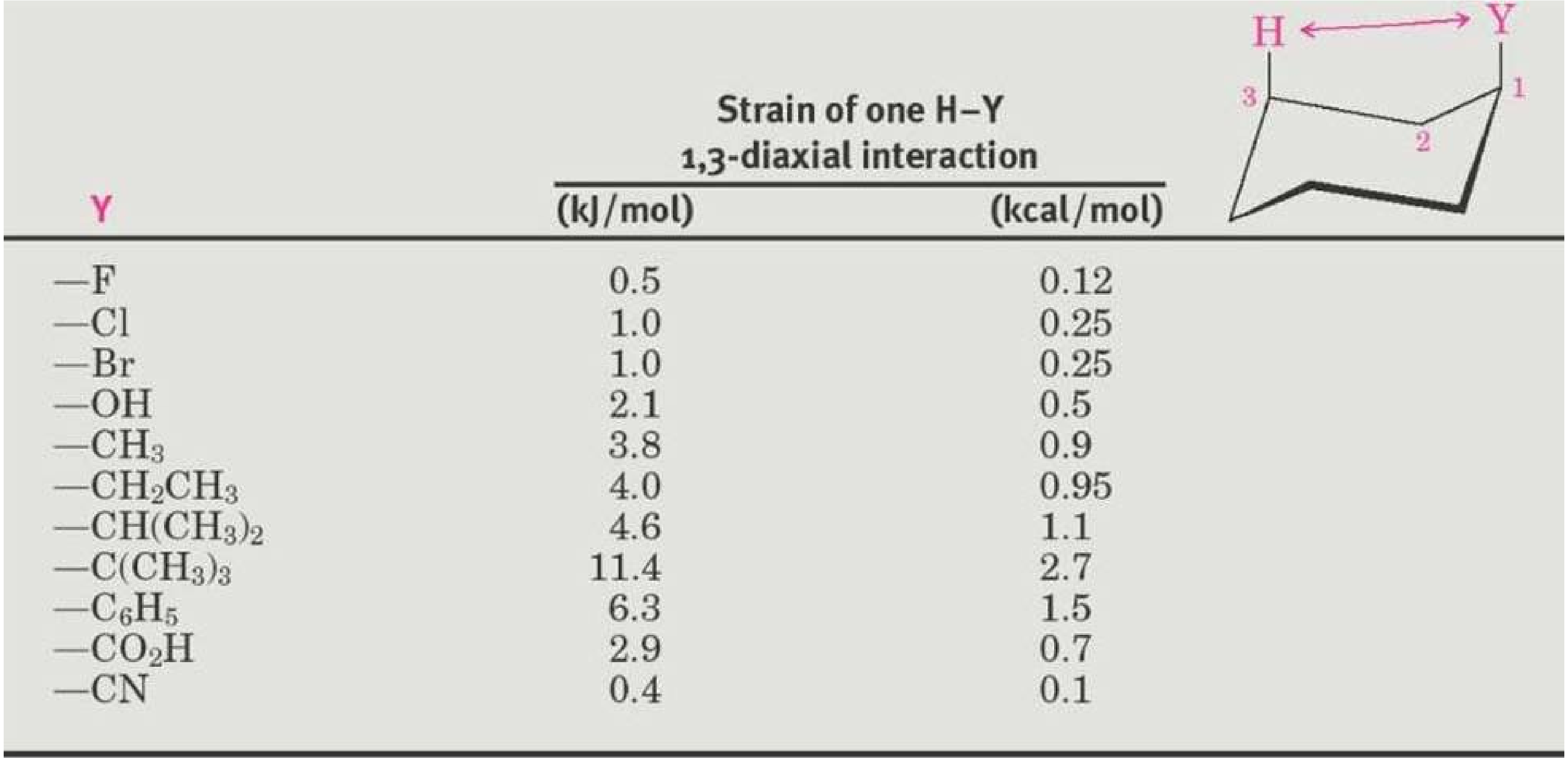






*anti*

# Steric Strain in Mono-substituted Cyclohexanes



| Y | Strain of one H–Y 1,3-diaxial interaction (kJ/mol) | Strain of one H–Y 1,3-diaxial interaction (kcal/mol) |
|---|---|---|
| —F | 0.5 | 0.12 |
| —Cl | 1.0 | 0.25 |
| —Br | 1.0 | 0.25 |
| —OH | 2.1 | 0.5 |
| —$CH_3$ | 3.8 | 0.9 |
| —$CH_2CH_3$ | 4.0 | 0.95 |
| —$CH(CH_3)_2$ | 4.6 | 1.1 |
| —$C(CH_3)_3$ | 11.4 | 2.7 |
| —$C_6H_5$ | 6.3 | 1.5 |
| —$CO_2H$ | 2.9 | 0.7 |
| —CN | 0.4 | 0.1 |

The relative population of the two chair conformers can be calculated by the equation,

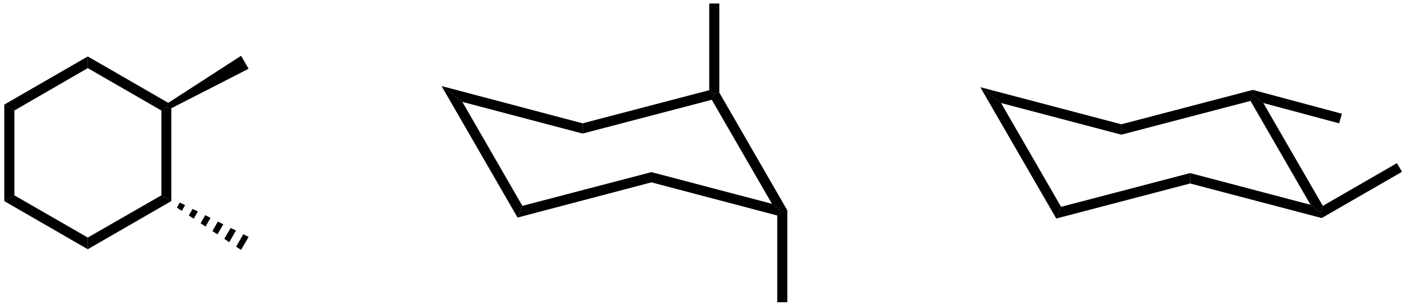
$$\Delta G = -RT \ln K_{eq}$$

For methylcyclohexane, the concentration of the equatorial form is almost 95%, while for *tert*-butylcyclohexane the equatorial conformer is present in 99.99% at room temperature.

# Di-substituted Cyclohexanes

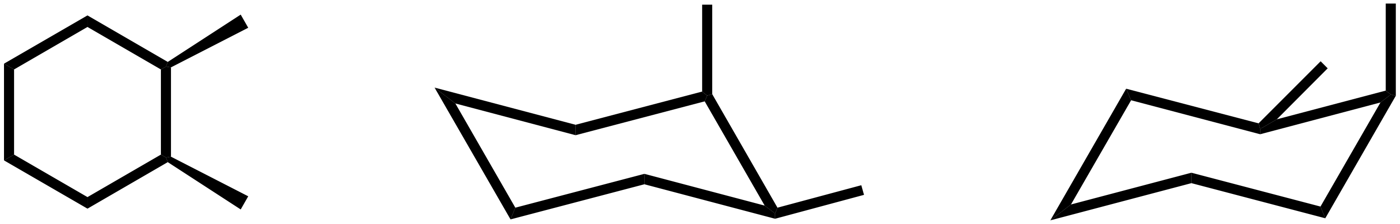
Relative orientation of two substituents in a cycloalkane are represented by *cis and trans* notations.

### *trans*-1,2-dimethylcyclohexane



The di-axial conformer is unstable by 4 × 0.9 = 3.6 kcal/mol
The two equatorial methyl groups in the di-equatorial conformer are gauche to each other and has a destabilizing interaction amounting to 0.9 kcal/mol

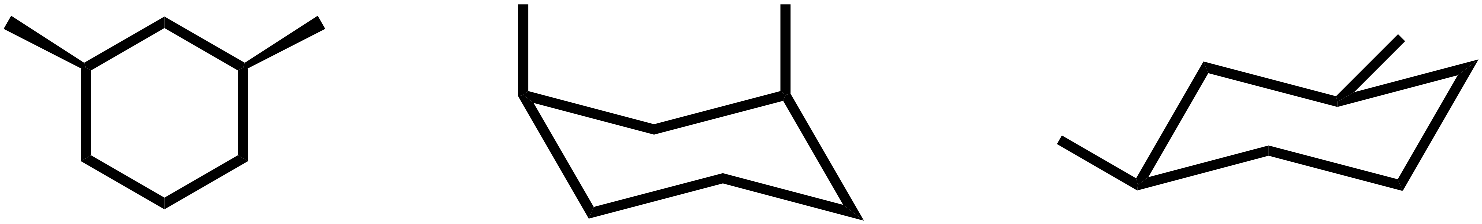
### *cis*-1,2-dimethylcyclohexane



Both the conformers are destabilized by 1.8 + 0.9 = 2.7 kcal/mol

# Di-substituted Cyclohexanes

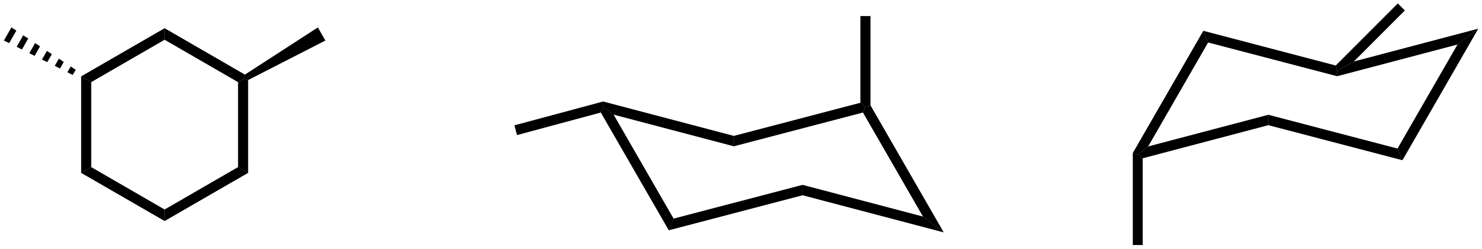
## *cis*-1,3-dimethylcyclohexane



The di-axial conformer is very unstable due to two $CH_3$ being in axial positions at the same side.

The di-equatorial conformer has no gauche butane interactions and is stable.

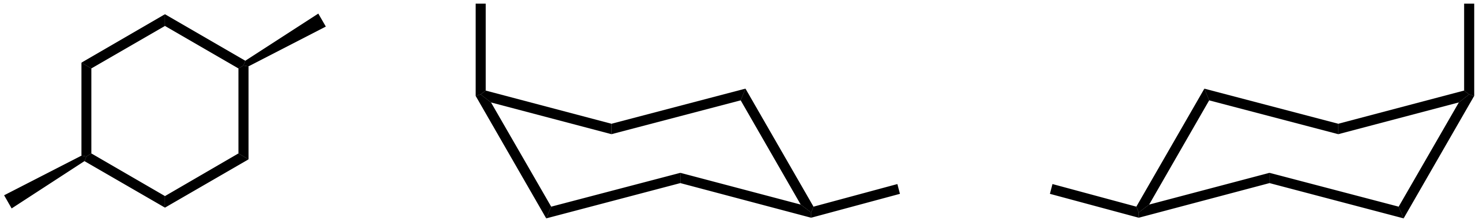
## *trans*-1,3-dimethylcyclohexane



Both the conformers are destabilized by 1.8 kcal/mol

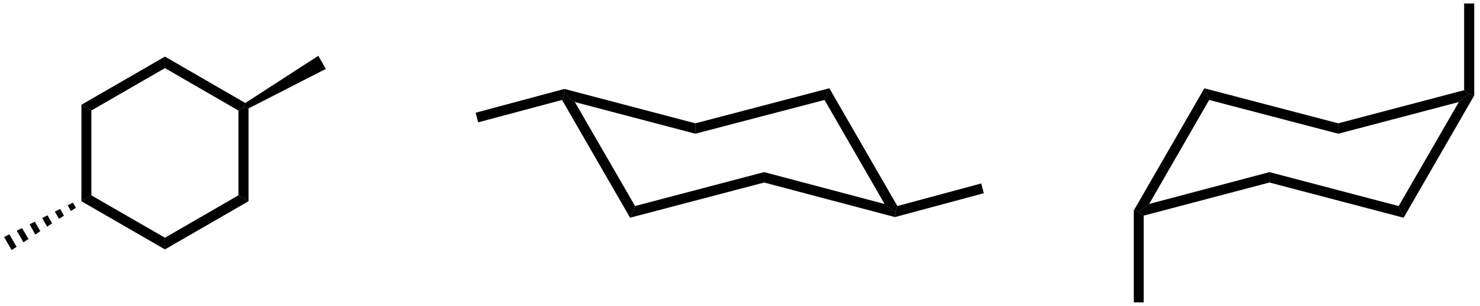
# Di-substituted Cyclohexanes

## *cis*-1,4-dimethylcyclohexane



Both the conformers are destabilized by 1.8 kcal/mol

## *trans*-1,4-dimethylcyclohexane



The di-axial conformer is unstable by 4 × 0.9 = 3.6 kcal/mol
The di-equatorial conformer has no gauche butane interactions and is stable.