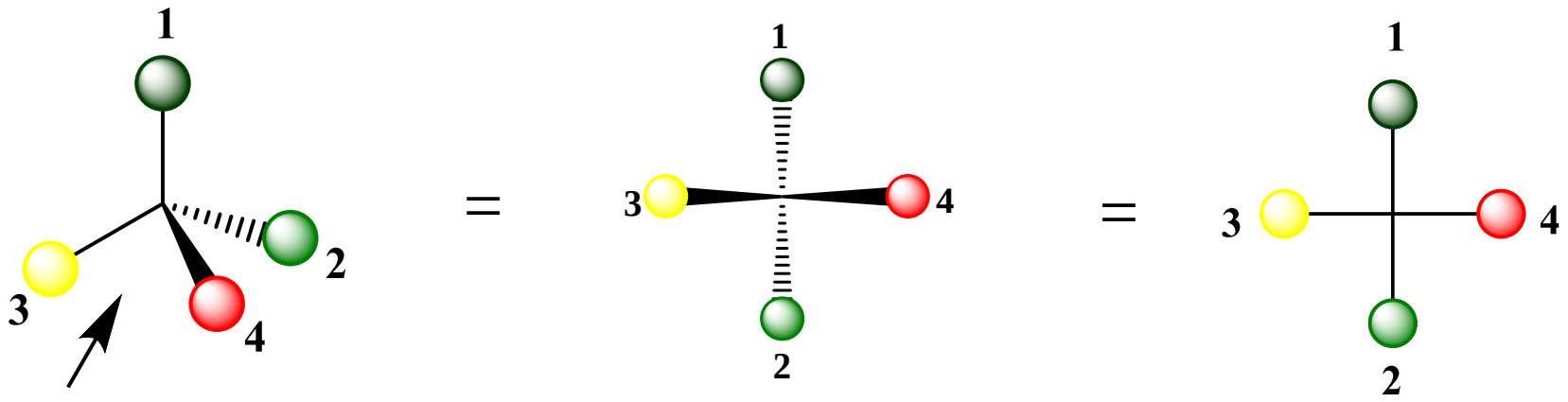
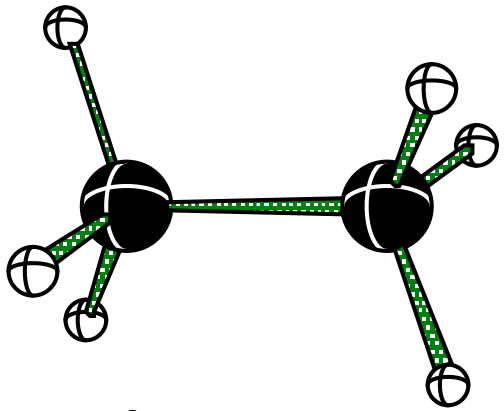
Recap

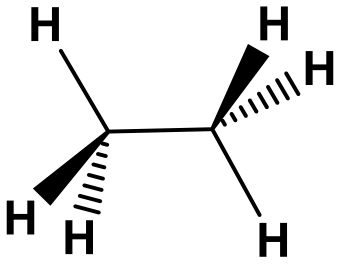


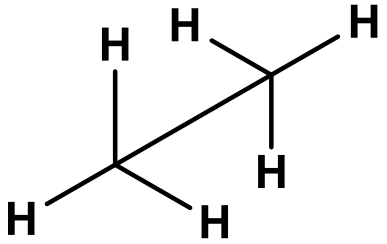
Fischer Projection

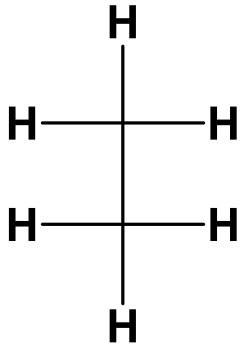
Various representations

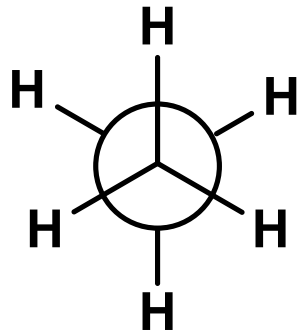


Ethane – 3D





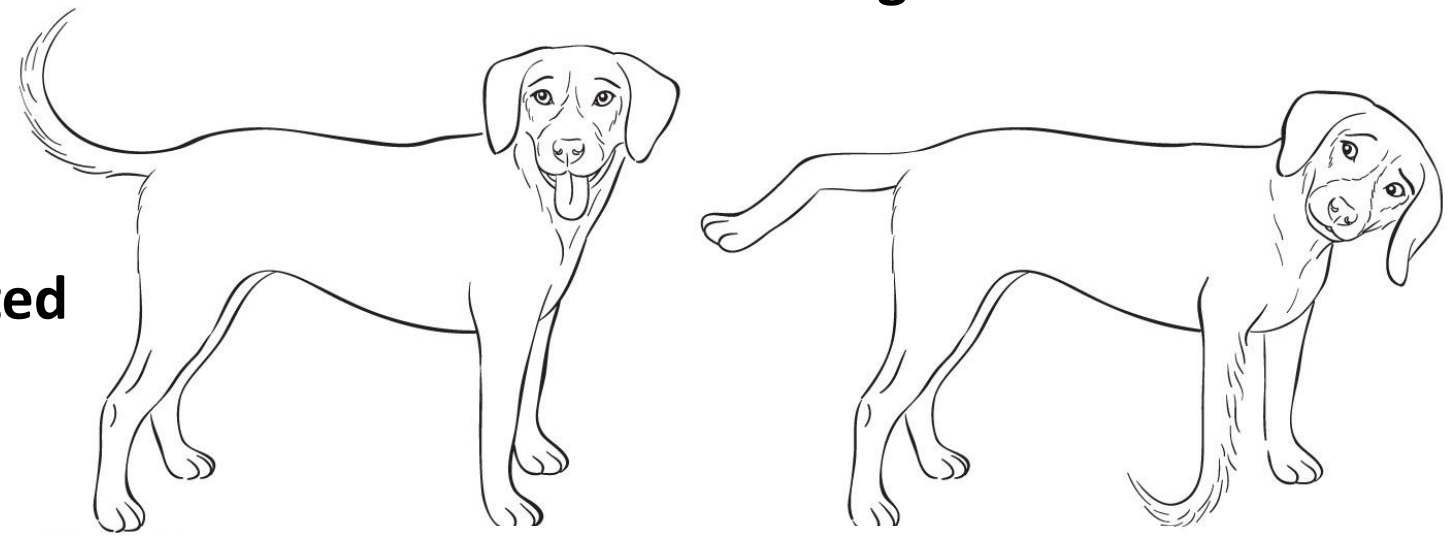




Configurations & Conformations

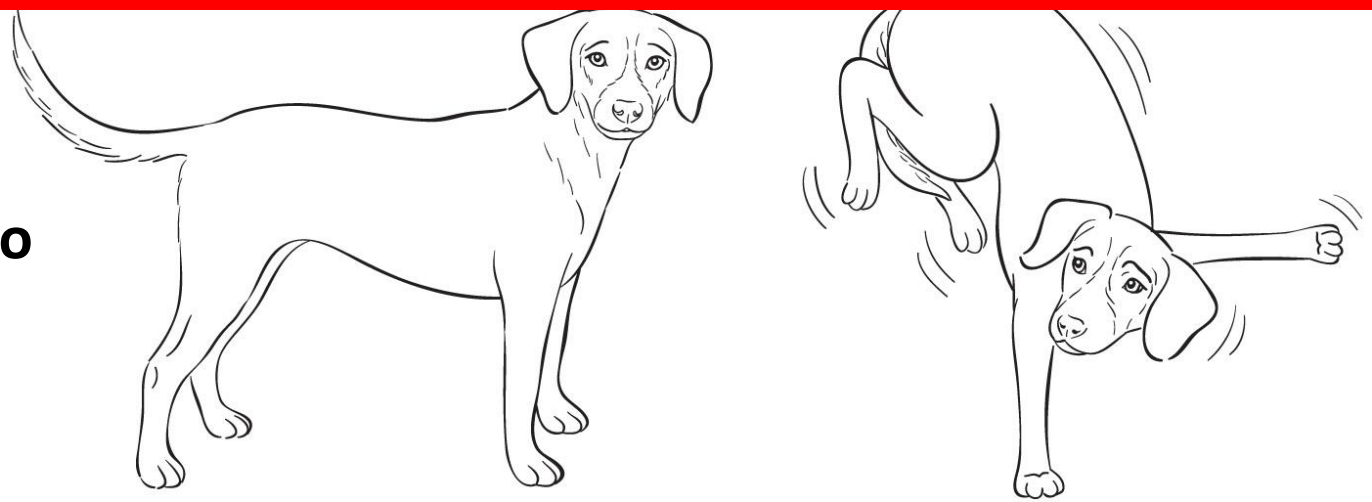
Different configurations

Can be separated



No animals were harmed in the making of this slide

Difficult to separate



Stable

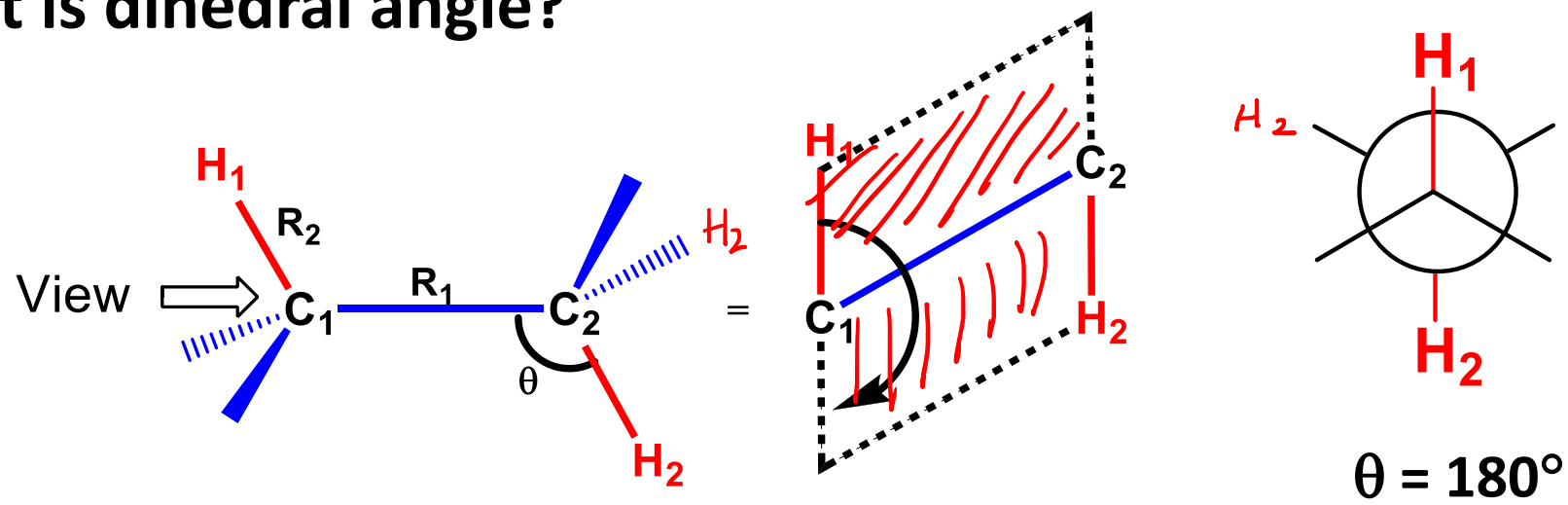
Unstable

Conformational Analysis

Conformational Analysis is the study of energetics of different conformers

Energy versus torsional angle (dihedral angle)

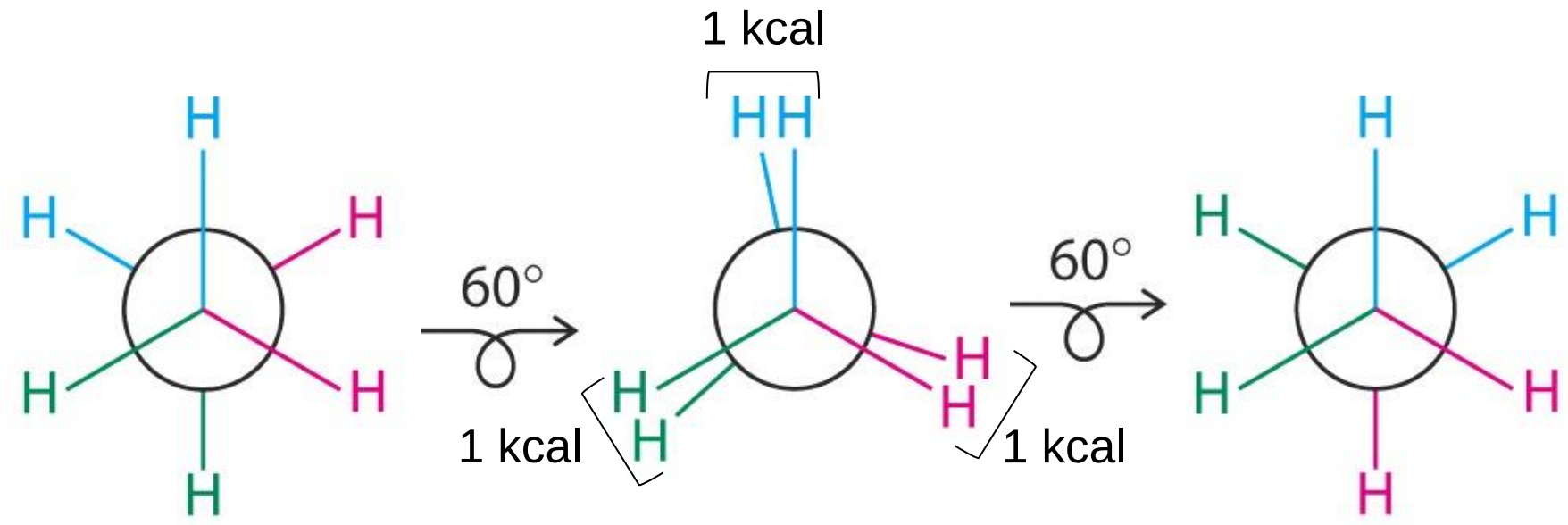
What is dihedral angle?



Bond length	between 2 atoms
Bond angle	between 3 atoms
Dihedral angle	between 4 atoms

Conformational Analysis - Ethane

Ethane has two major conformers – Staggered and Eclipsed



Staggered (S) **Eclipsed (E)** **Staggered (S)**

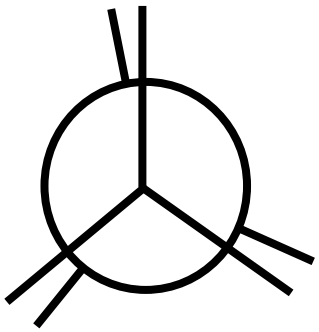
The eclipsed conformation of ethane is 3 kcal/mol less stable than the staggered conformation. (1 kcal/mol for each eclipsed H/H pair)

Rotation Around Bonds is Not "Free"
Barrier to rotation here 3 kcal/mol

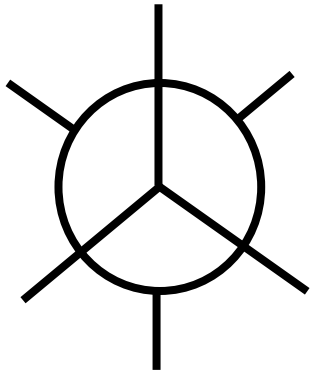
Rotational Barrier in Ethane

Barrier of 3 kcal mol^{-1} due to steric and electronic effects

Transition state is eclipsed

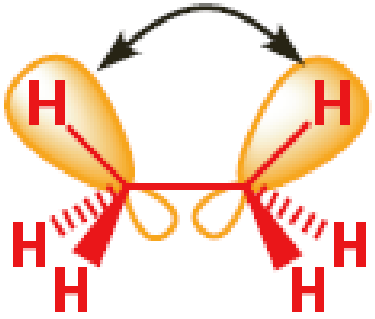


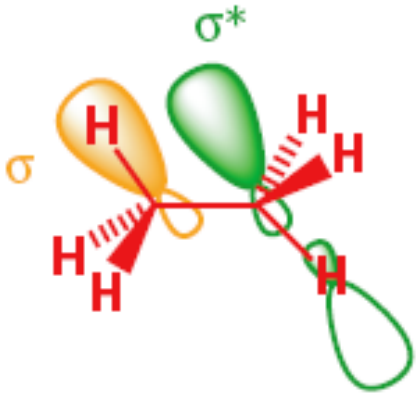
Most stable conformer is staggered



eclipsed:

filled orbitals repel

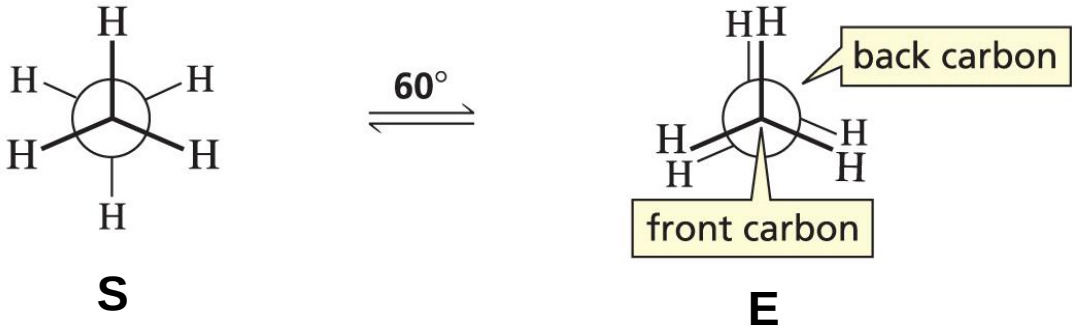




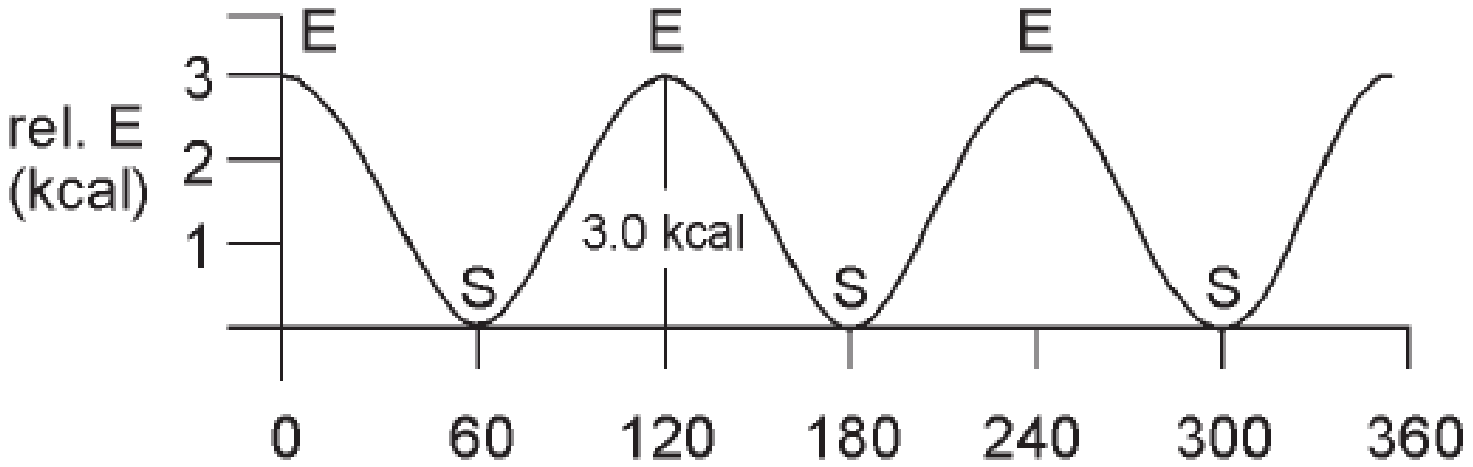
and empty C–H σ* antibonding orbital

Conformational Analysis - Ethane

Eclipsed conformer is 3.0 kcal/mol higher in energy than the staggered conformer: eclipsing interactions H/H (1.0 kcal)



S E



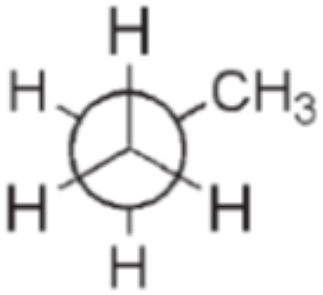
Small Activity

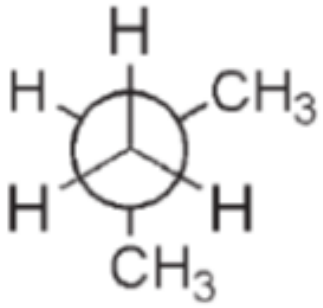
Calculate the barrier of rotation for propane, 2-methyl propane and 2,2-dimethyl propane

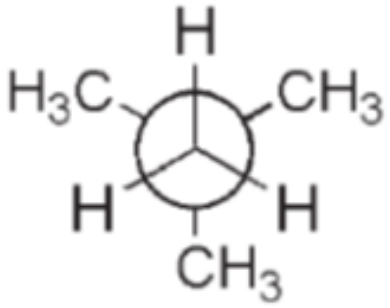
Eclipsing interactions H/H (1.0 kcal) and Me/H (1.3 kcal)

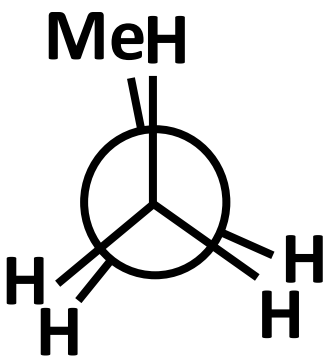
Check your Answers

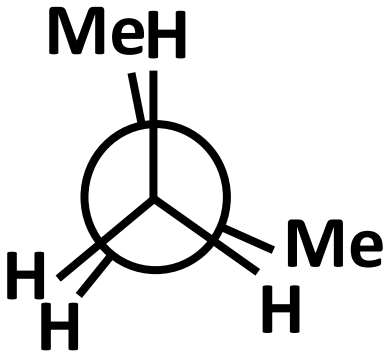
Eclipsing interactions H/H (1.0 kcal) and Me/H (1.3 kcal)

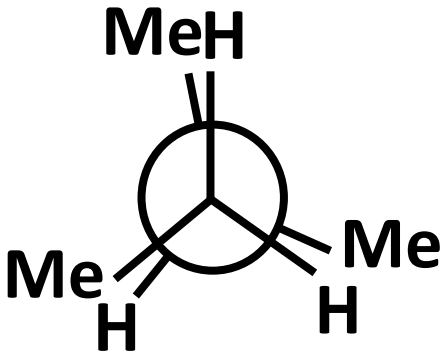








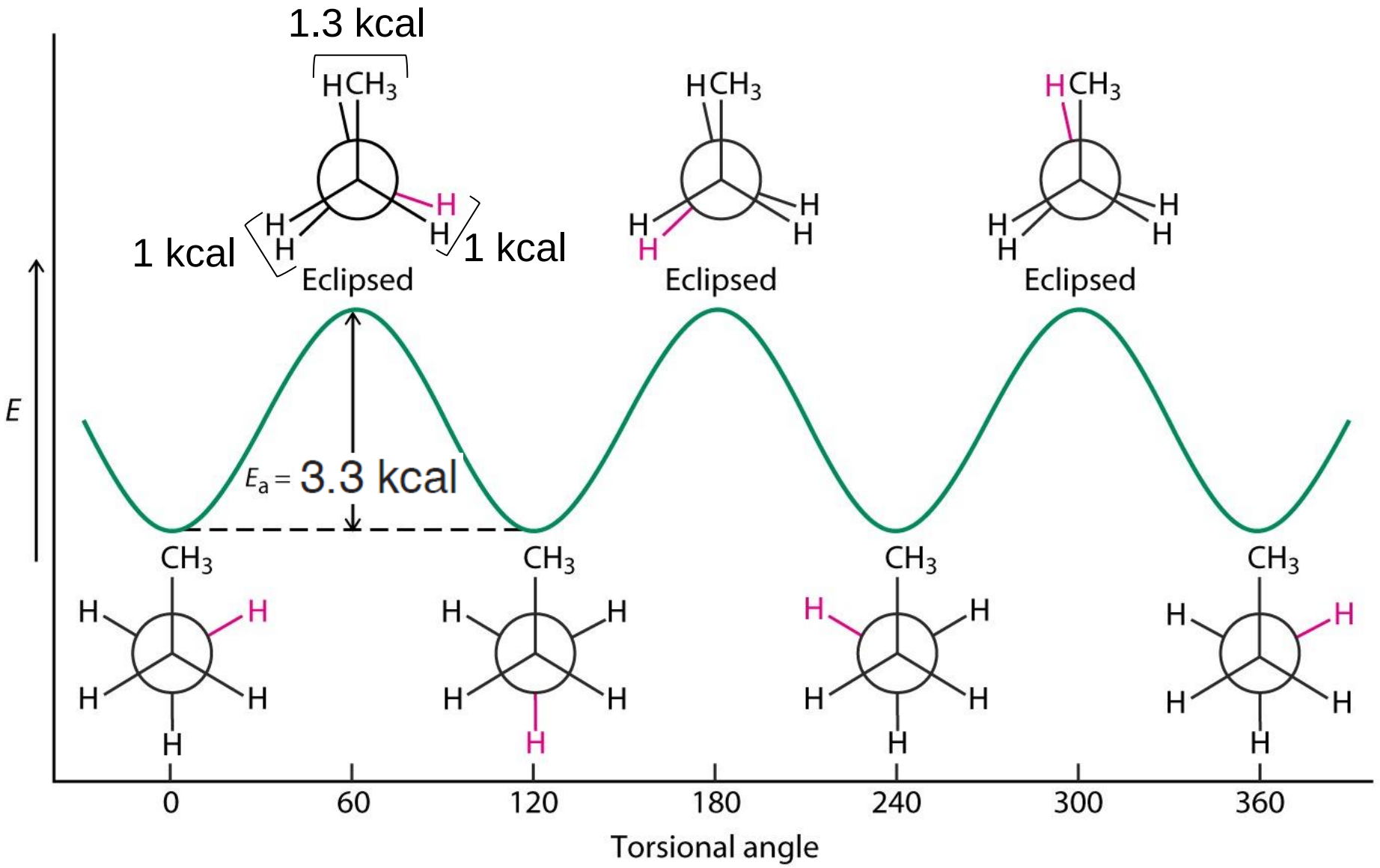




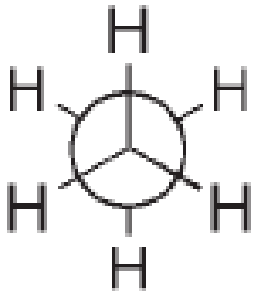
Calculated	3.3 kcal/mol	3.6 kcal/mol	3.9 kcal/mol
Observed	3.4 kcal/mol	3.9 kcal/mol	4.7 kcal/mol

Conformational Analysis - Propane

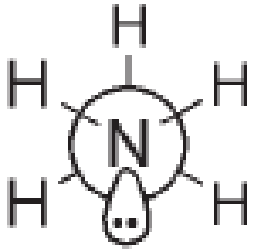
Note: eclipsing interactions H/H (1.0 kcal) and Me/H (1.3 kcal)



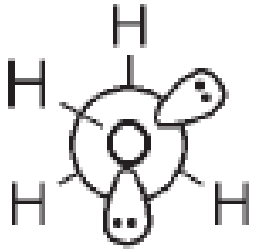
Lone Pairs Are Not Bad!



3 kcal

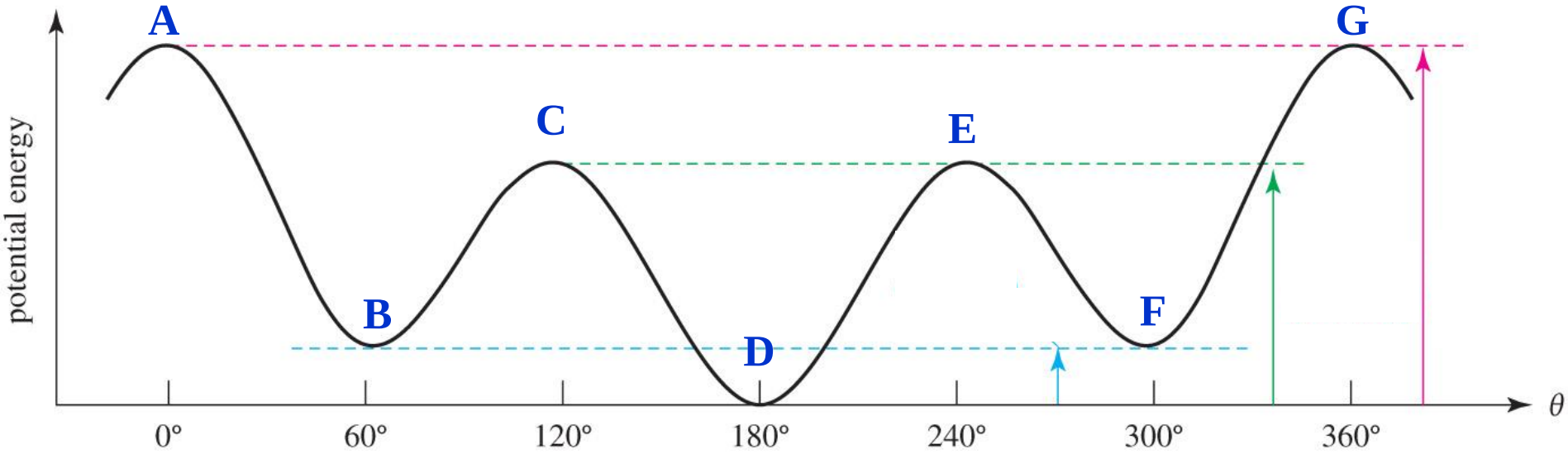


2 kcal

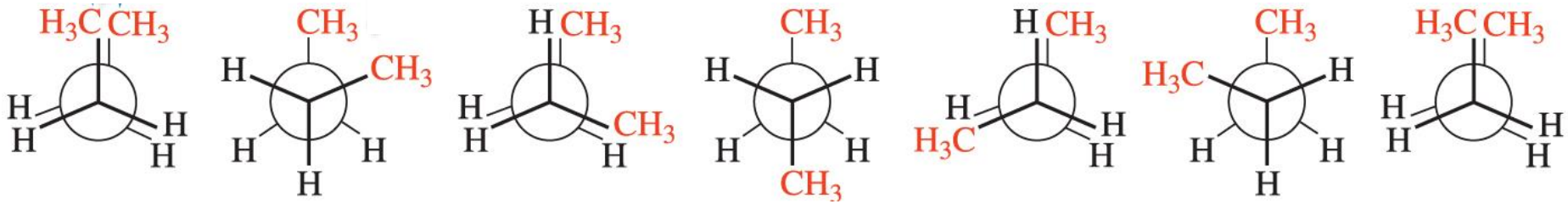


1 kcal

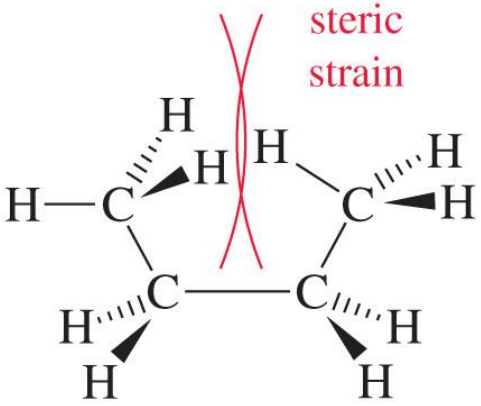
Conformational Analysis - Butane

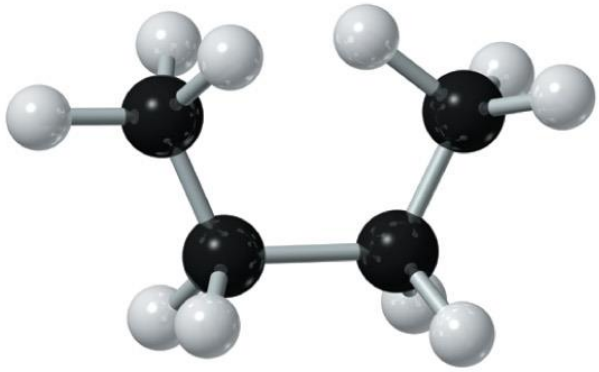


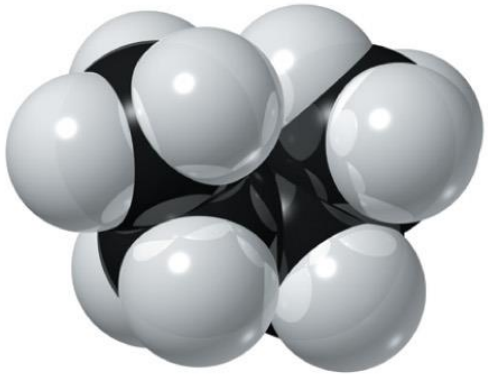
6 kcal totally eclipsed	0.9kcal gauche	3.6 kcal eclipsed	lowest anti	3.6 kcal eclipsed	0.9kcal gauche	6 kcal totally eclipsed



Steric Strain







Totally eclipsed conformation of butane

- The totally eclipsed conformation is higher in energy because it forces the two end methyl groups so close together that their electron clouds experience a strong repulsion

- This kind of interference between two bulky groups is called ***steric strain*** or ***steric hindrance***

Types of Molecular Strain

Torsional Strain: Extra energy of eclipsed conformation arising due to the repulsion between bonding electrons of one substituent with that of the other as they pass close to each other

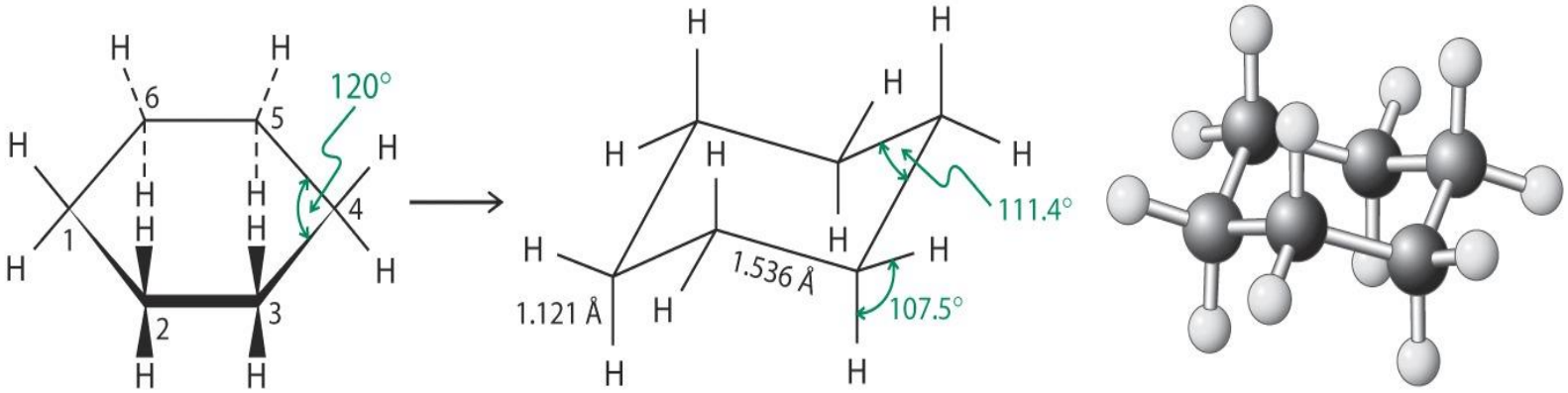
Steric Strain: Strain induced when two atoms or groups in a molecule are too close to each other, arising due to repulsion between electron clouds of interacting atoms/groups

Angle Strain: Strain induced in molecules when the bond angles are different from the desired tetrahedral bond angle of 109.5°

Cyclohexane

Both angle and torsional (eclipsing interactions) strains can be avoided by ring puckering.

Ring puckering leads to "CHAIR" and "BOAT" conformers



A

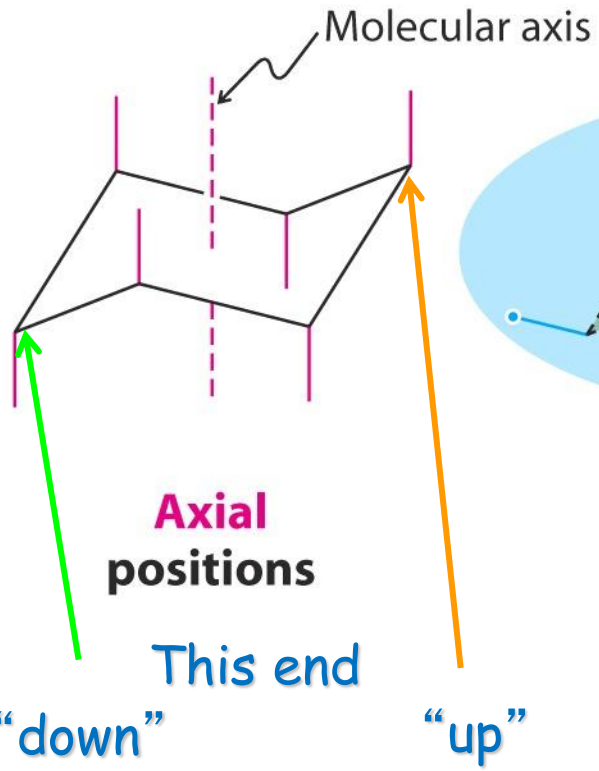
Planar cyclohexane
(120° bond angles;
12 eclipsing hydrogens)

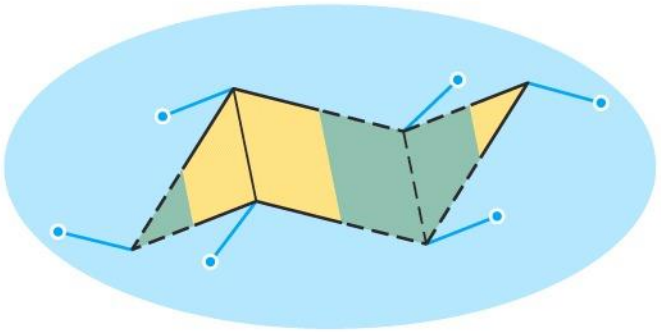
B

Chair cyclohexane
(Nearly tetrahedral bond angles;
no eclipsing hydrogens)

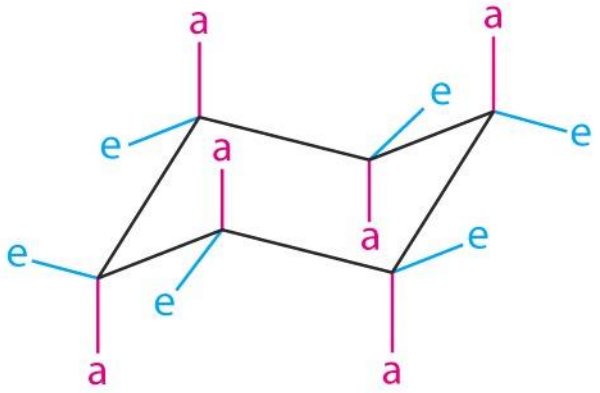
C

Drawing Chair form





Equatorial
positions

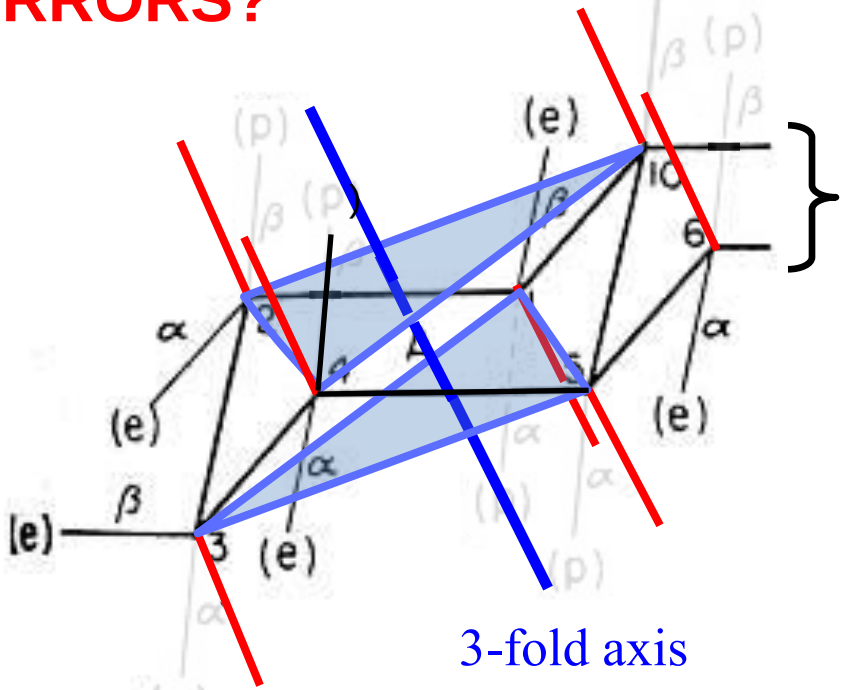


Axial (a) and equatorial (e)
positions

Equatorial bonds must be *parallel* to the C–C bond(s) "one over"
[not the attached one(s), but the next one(s)]

D.H.R. Barton Invents *Conformational Analysis* (1950)

ERRORS?



β ⇒ "up" ; α ⇒ "down"

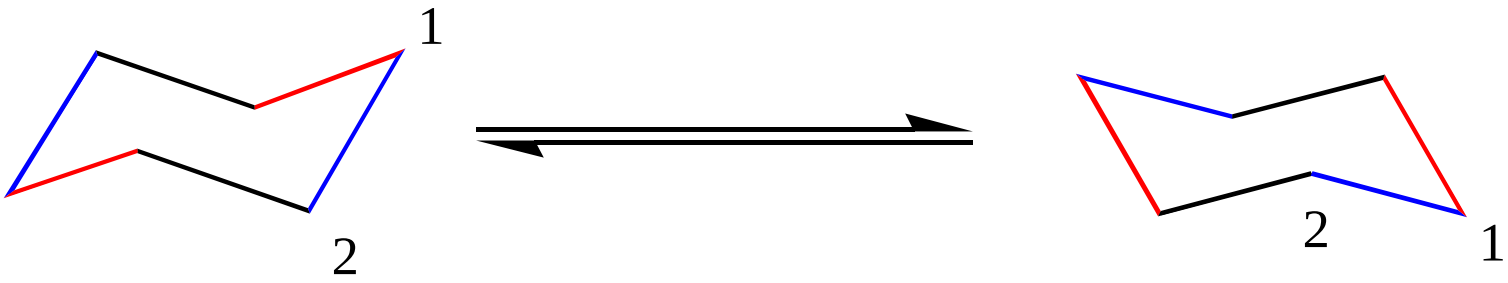
(for molecule in conventional orientation, old-fashioned configuration notation, like *cis / trans*)

(e) *"equatorial"*

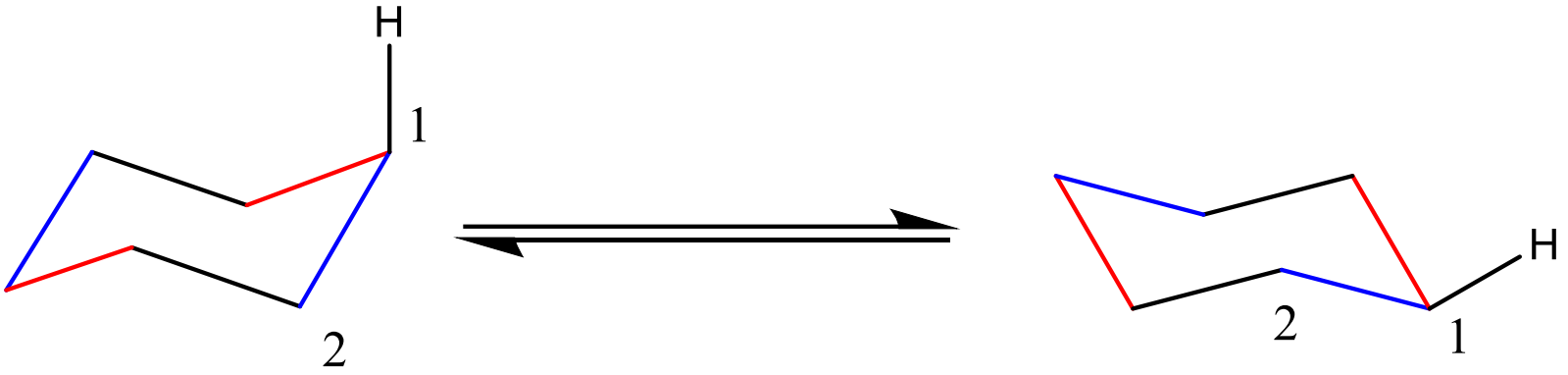
(p) *"polar"* (now *axial*)

(Nobel Prize 1969 for "development of the concept of conformation and its application in chemistry")

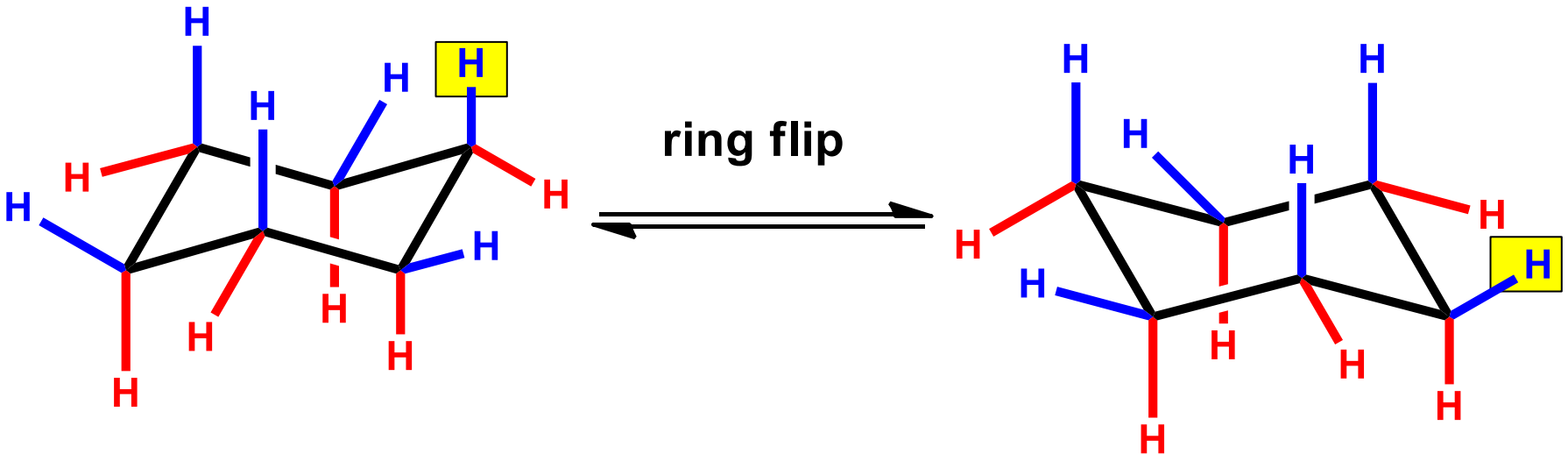
Ring Flipping in Cyclohexane



H_{ax} and H_{eq} are distinguishable at very low temp.

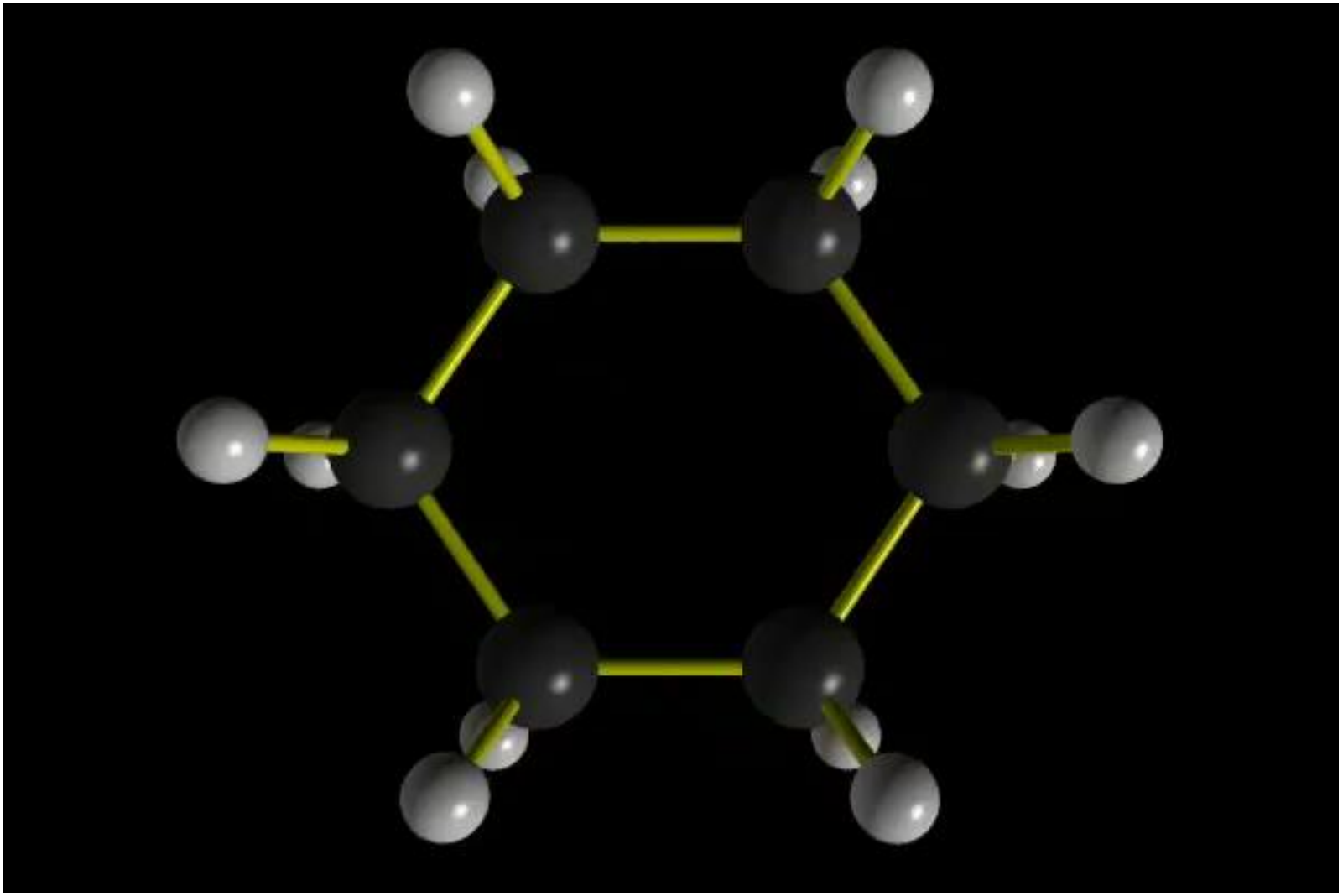


The Ring Flip Causes Equatorial-Axial Exchange



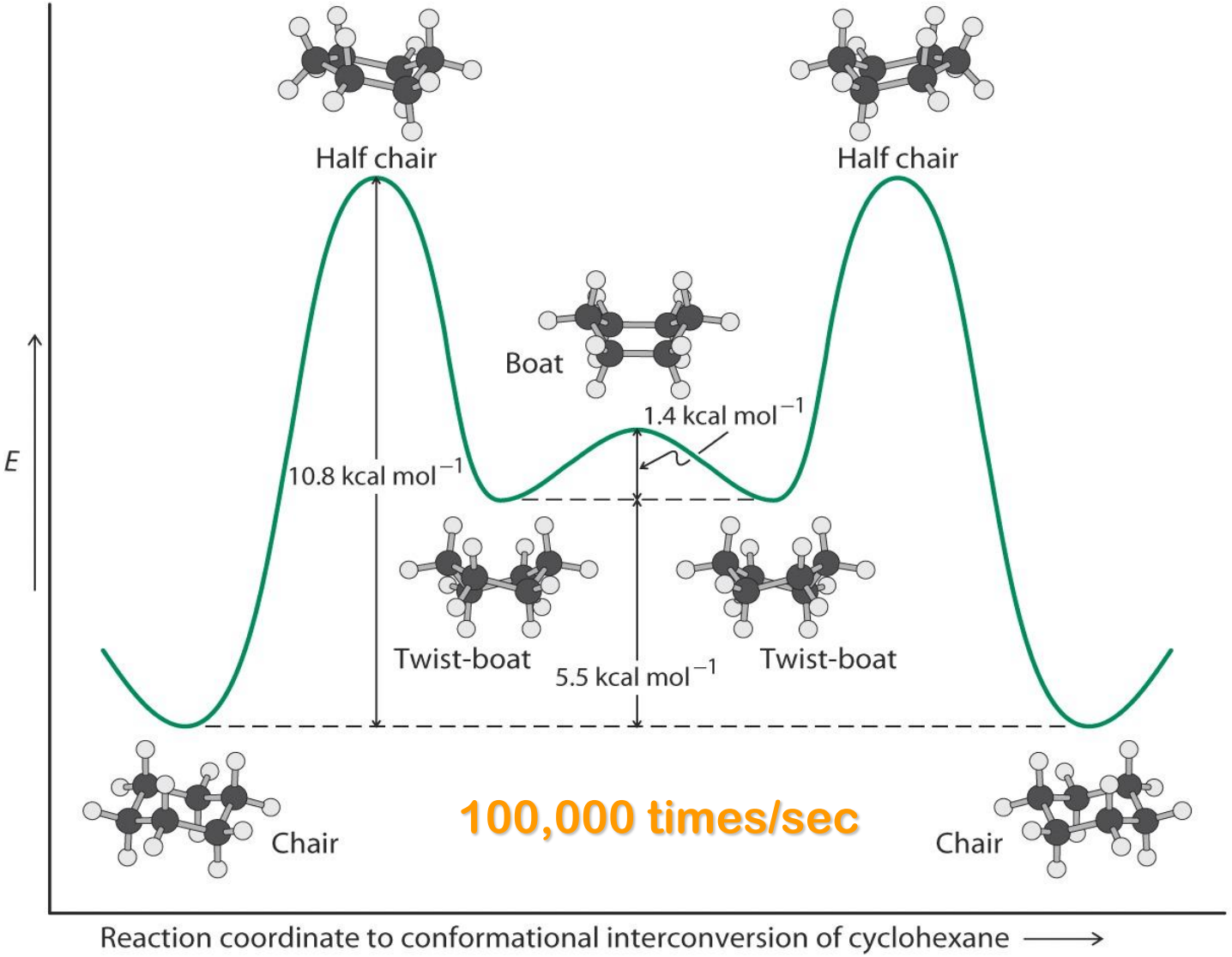
The two structures are the same!

Ring Flip



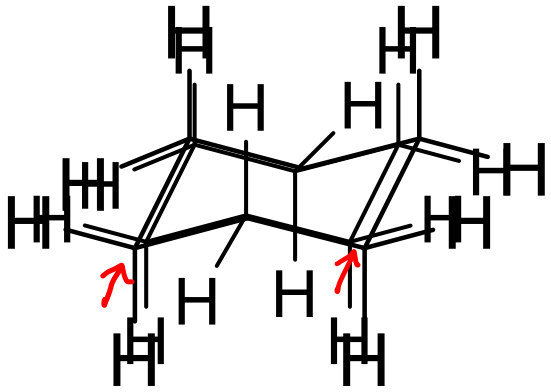
Ring Flipping - Energetics

In monosubstituted (small groups) cyclohexanes the ring flipping is of the order of 10^4 to 10^5 inversions/second

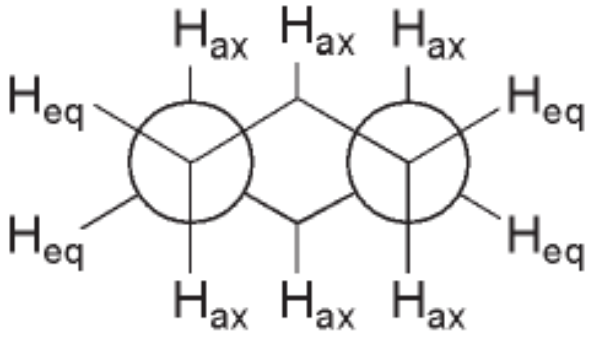


Chair v/s Boat : Newman Projection

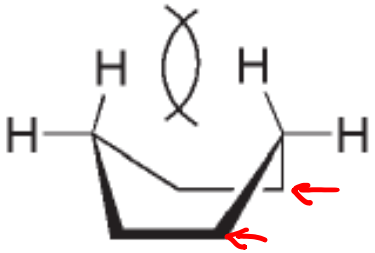
Chair



Staggered form

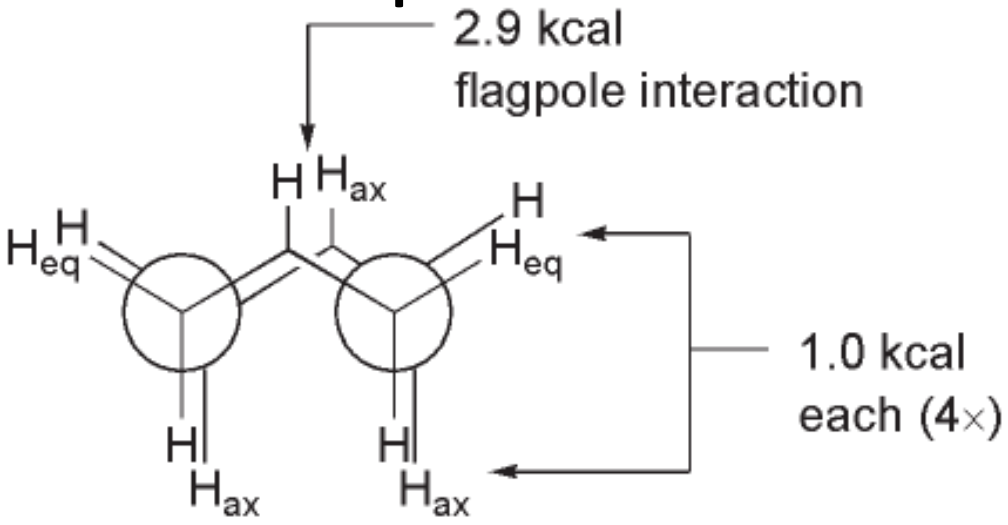


Boat



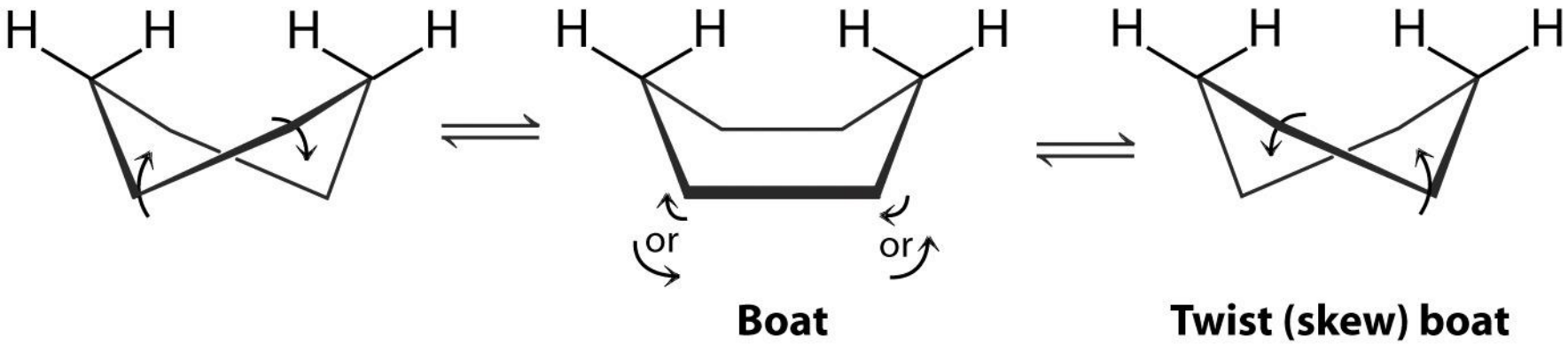
≡

Eclipsed form



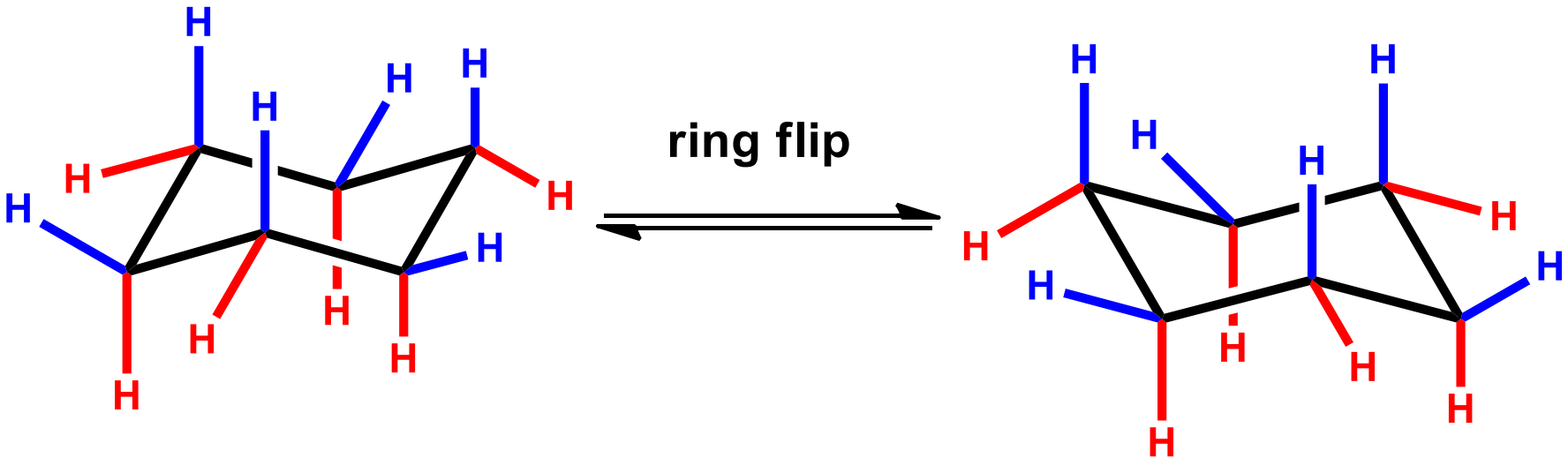
Rel E = 6.9 kcal

Relief by Twisting



But this is only part of its mobility. The molecule "flips" from one chair to another chair form.

Ring Flip - Summary



The two structures are the same.
What happens in substituted cyclohexanes?