

CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture 30 (04-04-2018)

Isomers: The Same But Not The Same

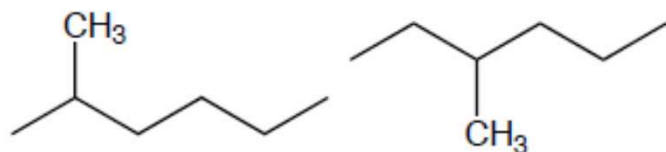


Constitutional or structural isomers

The compounds that have identical molecular formulas but different connectivity of atoms and properties:

- 1) Chain isomers.
- 2) Positional isomers.
- 3) Tautomers.

(Bond breaking required)



2-methylhexane

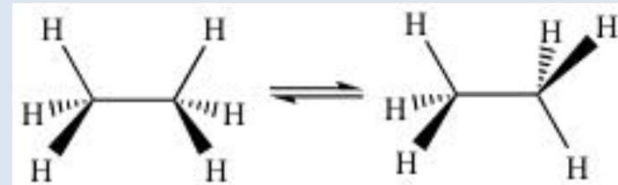
3-methylhexane

Stereoisomers (spatial isomers)

The compounds that have identical molecular formulas and same connectivity of atoms but different arrangement of atoms in space:

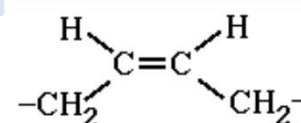
- 1) Conformational isomers (conformers).

Rotating about bonds (Bond breaking not required)

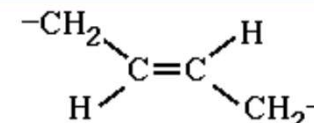


- 2) Configurational isomers: (Bond breaking required)

- Enantiomers.
- Diastereomers



cis

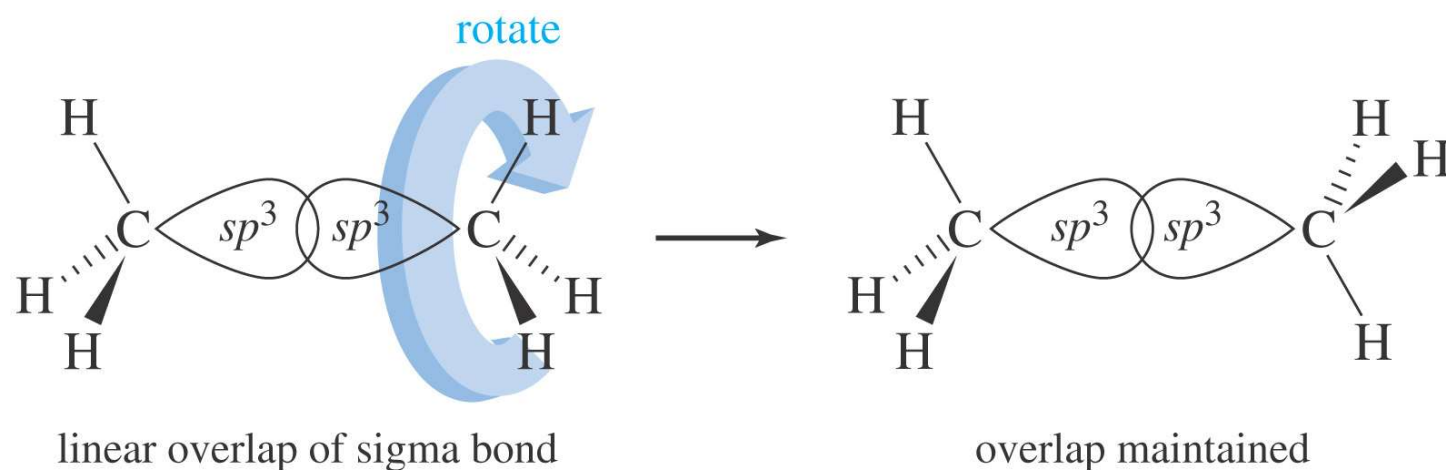


trans

CONFORMATIONS



- Two methyl groups in ethane are not fixed in a single position.
- They rotate about the sigma bond connecting two carbon atoms, maintaining the **linear bonding overlap**.
- The different arrangements formed by rotation about single bond are called **conformations** and a specific conformation is called a **conformer**.

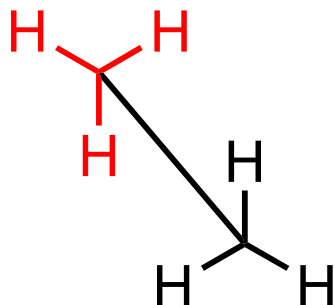
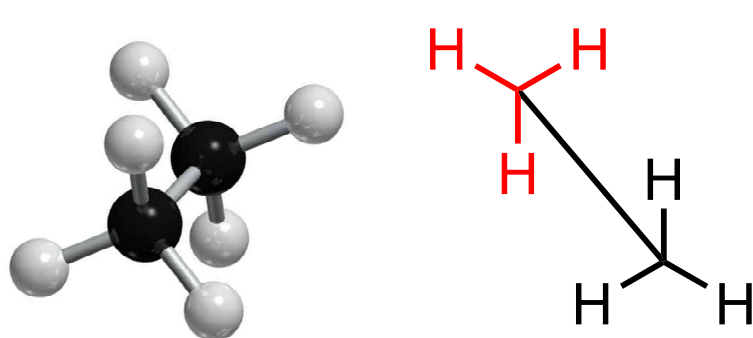


Since conformations differ from each other only in the way their atoms are oriented in space, they are **stereoisomers**.

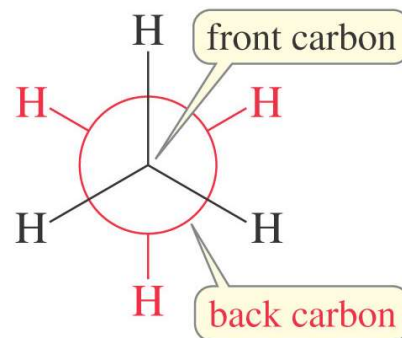
CONFORMATIONS



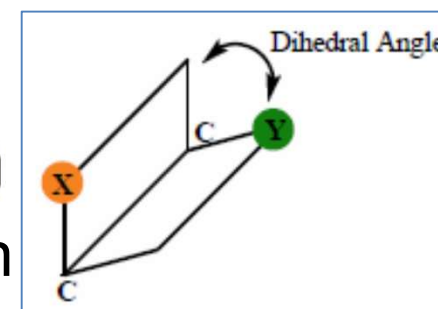
Conformations are represented by two kinds of formulas
(1) Sawhorse formula & (2) Newman projection formula



sawhorse



Newman projection

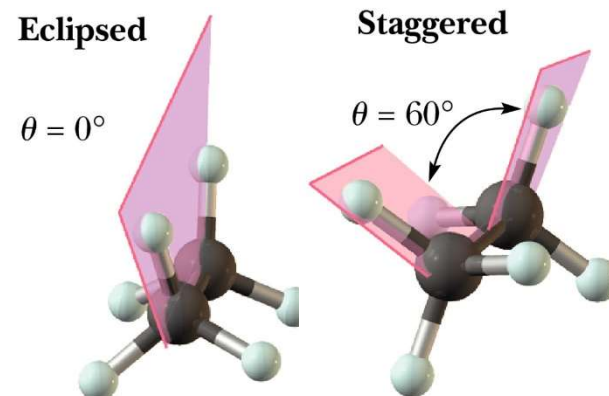
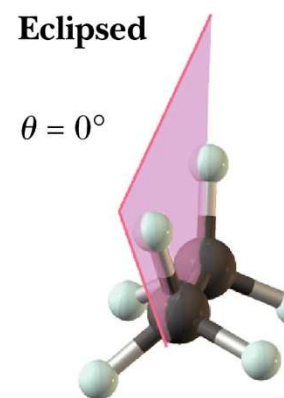


Dihedral angle (θ): Angle between the C-H bond on the front carbon atom and C-H bond on the back carbon atom in Newman projection.

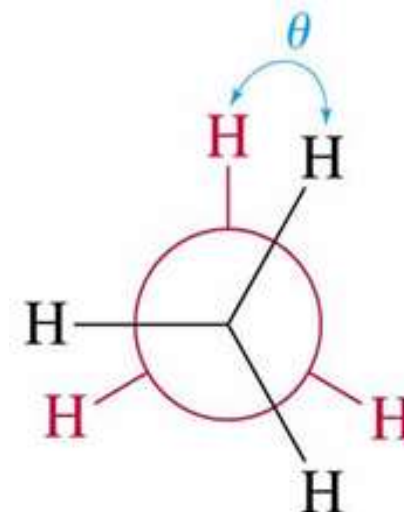
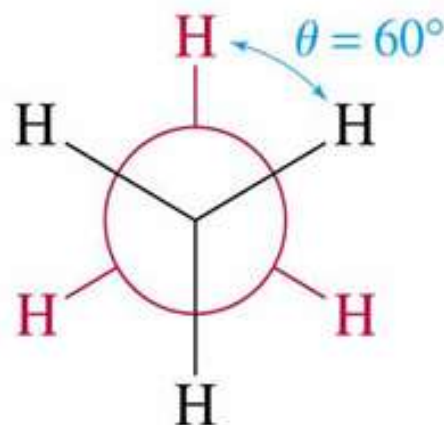
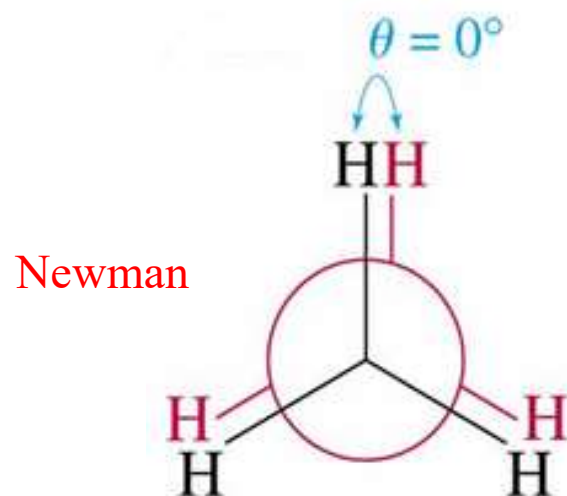
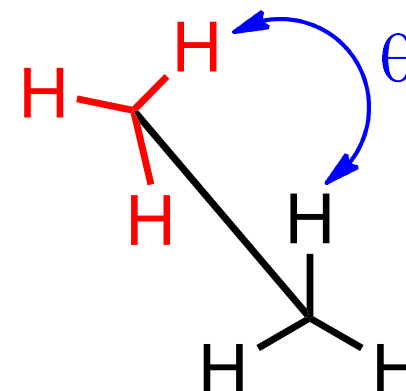
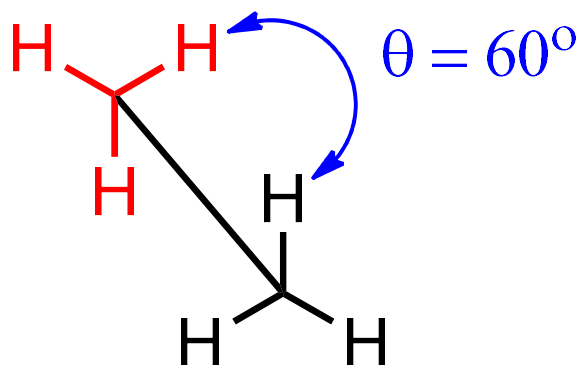
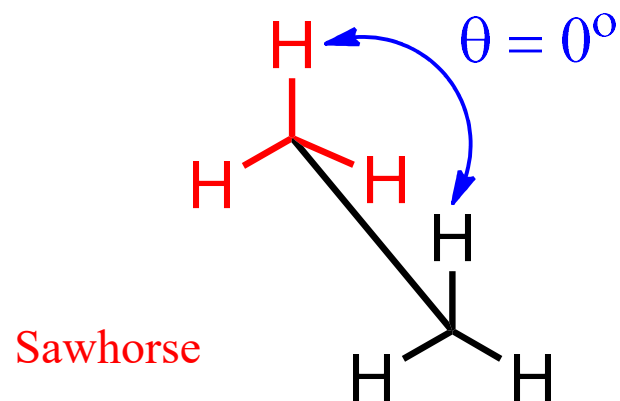
Eclipsed conformation: ($\theta = 0^\circ$)

Staggered conformation: ($\theta = 60^\circ$)

Skew conformation: ($\theta = \text{anything else}$)



CONFORMATIONS



Eclipsed

Staggered

Skew

CONFORMATIONS



Conformational analysis: study of energetics of different conformations.

Potential energy of the molecule:

Minimum for the staggered conformation

Increases with rotation

Maximum at the eclipsed conformation

Torsional Strain: It is the resistance to twisting (torsion) as molecule rotates toward an eclipsed conformation.

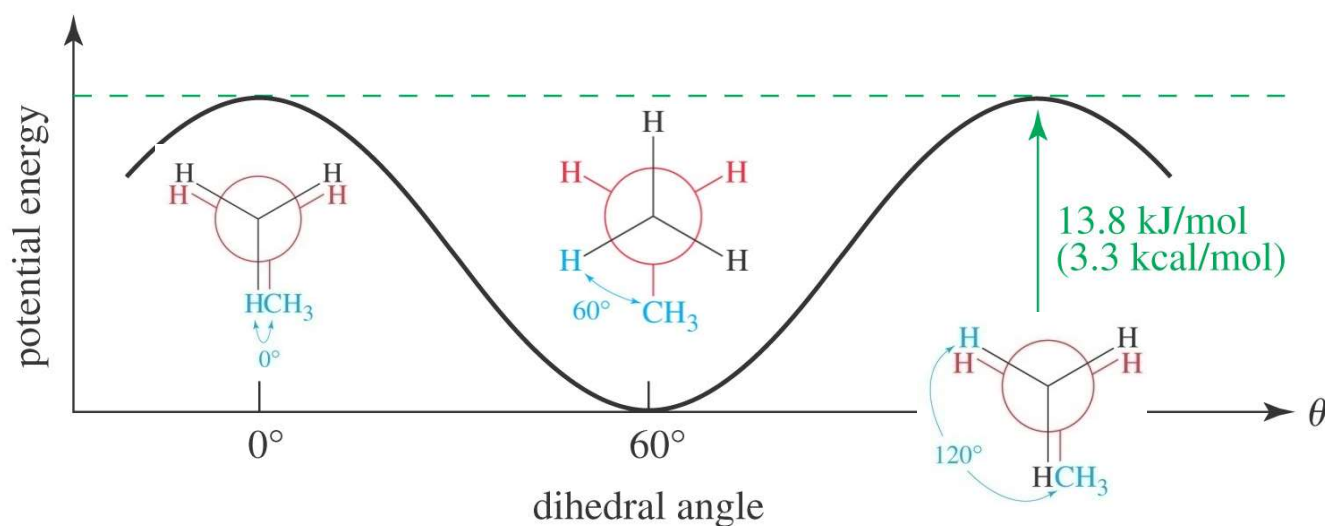
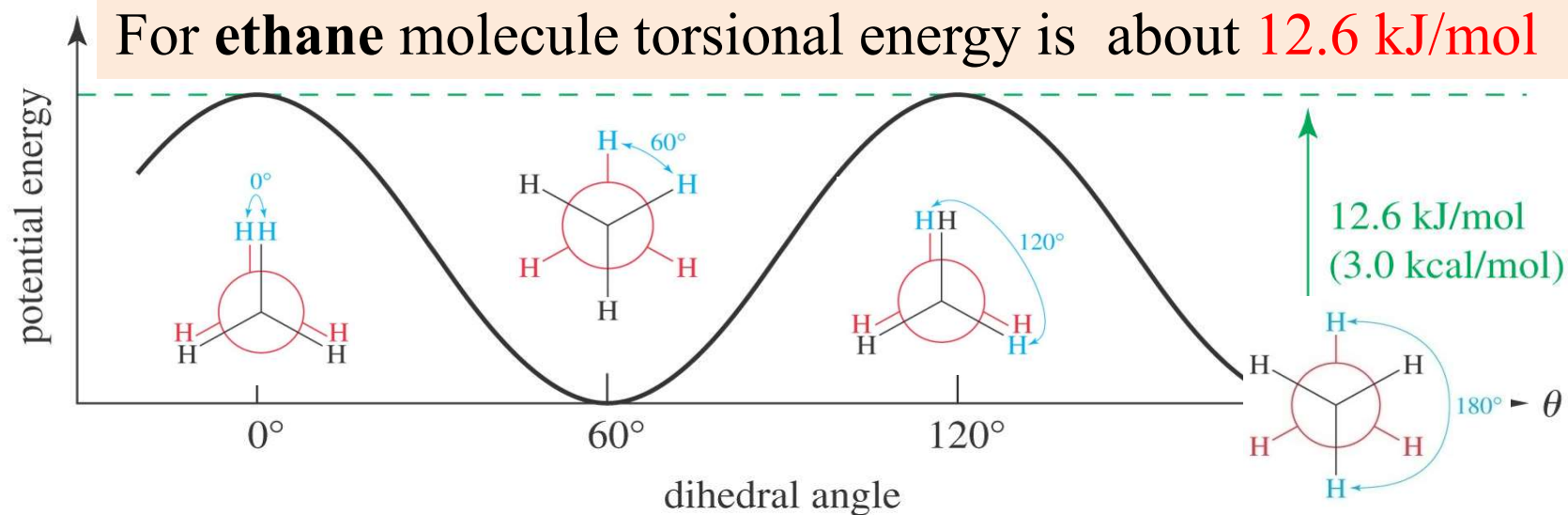
The energy difference between staggered and eclipsed conformers is called **torsional energy**.

At any given moment all molecules do not exist in most stable conformation; rather a higher percentage of molecules are present in a more stable conformation than any other arrangement.

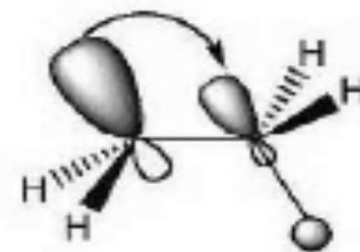
CONFORMATIONAL ANALYSIS



For **ethane** molecule torsional energy is about **12.6 kJ/mol**



Staggered



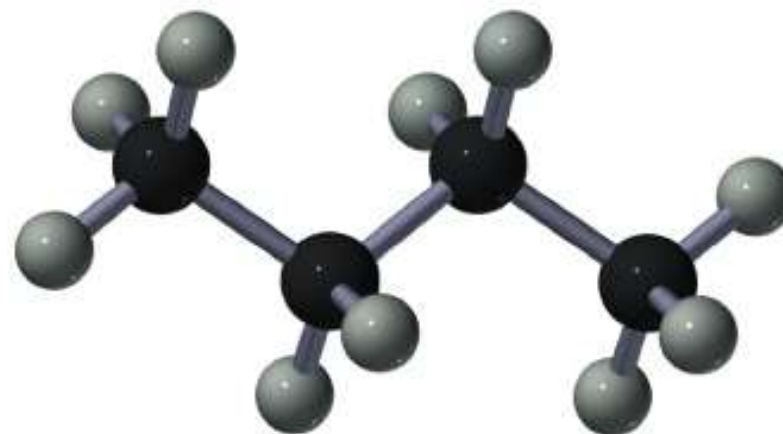
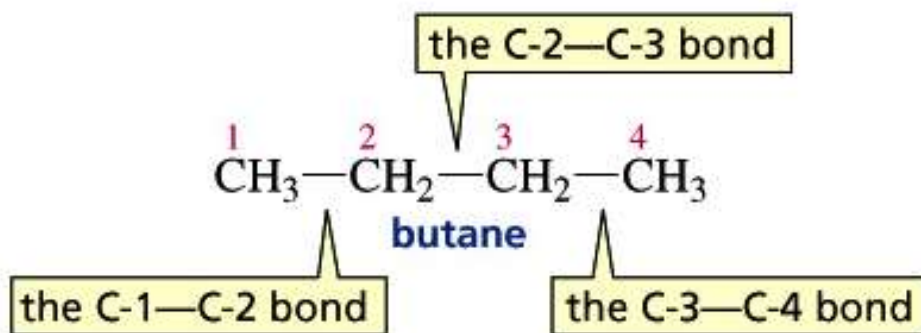
**Strengthened
Hyperconjugation
(attractive)**

For **propane** molecule torsional energy is about **13.8 kJ/mol**

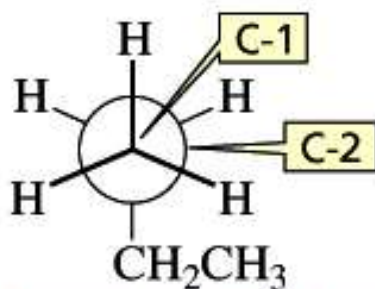
CONFORMATIONAL ANALYSIS OF n-BUTANE



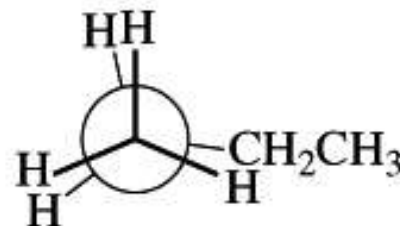
Rotation about the C₂-C₃ single bond



ball-and-stick model of butane



staggered conformation for rotation about the C-1—C-2 bond in butane



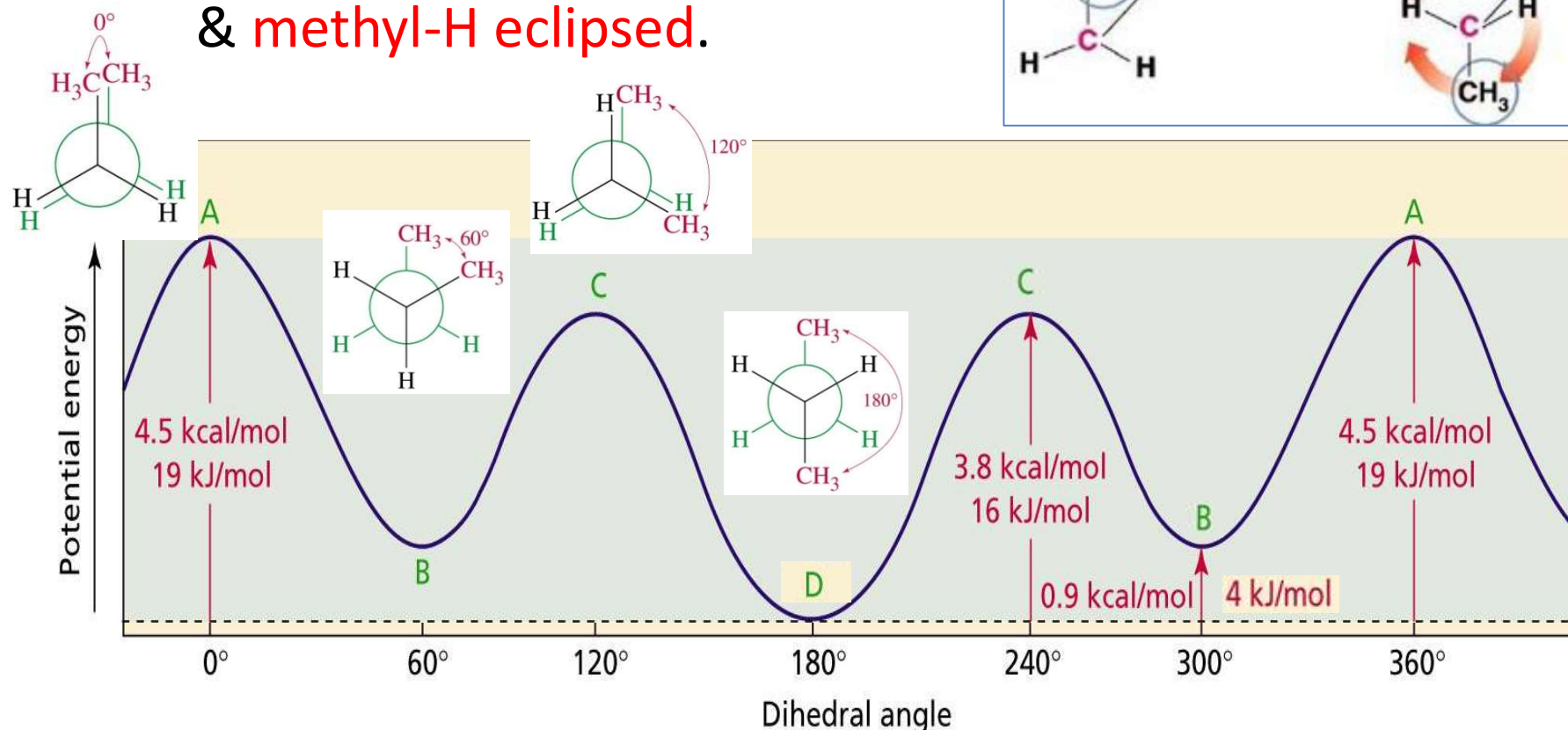
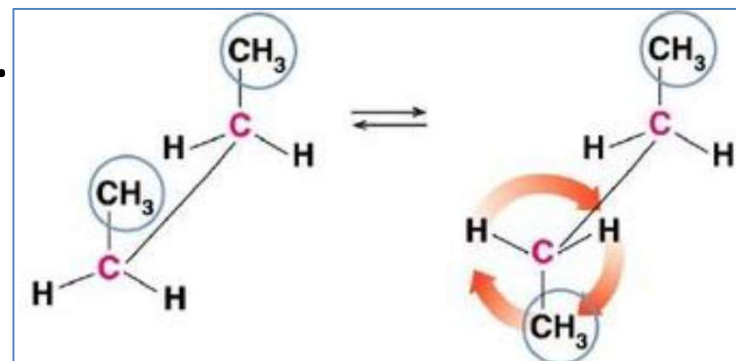
eclipsed conformation for rotation about the C-1—C-2 bond in butane

CONFORMATIONAL ANALYSIS



Free rotation around C2-C3 bond in n-butane

- Highest energy has methyl groups **eclipsed**.
- Lowest energy has methyl groups **anti**.
- In between, **methyl-methyl gauche** & **methyl-H eclipsed**.



CONFORMATIONS

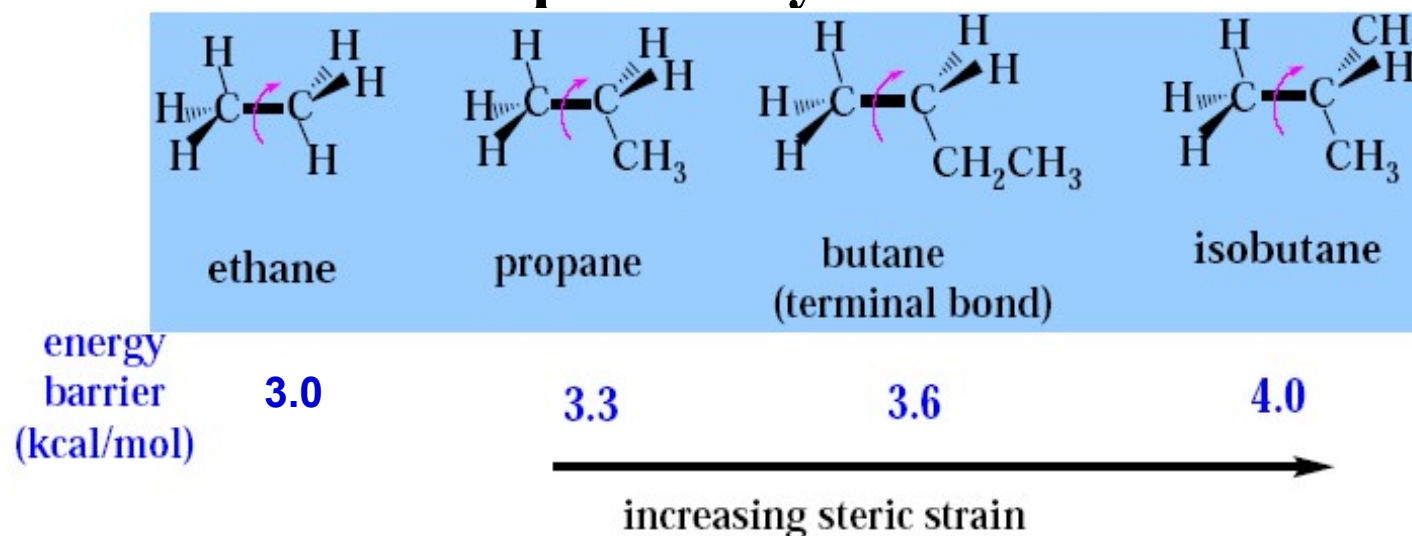


- Anti conformation is lowest in energy.
 - “Straight chain” actually is zigzag.
 - A staggered conformation with two larger groups 180° from each other is called **anti**.
 - A staggered conformation with two larger groups 60° from each other is called **gauche**.
- In most of the cases staggered conformations are lower in energy than the eclipsed conformations.
 - The relative energies of the individual staggered conformations depend on their steric strain.
 - **Steric strain** is an increase in energy resulting when atoms are forced too close to one another.
 - Gauche conformations are generally higher in energy than anti conformations because of **steric strain**.

CONFORMATIONAL ANALYSIS



- Increase in **torsional strain** (from ~ 12.6 kJ/mol to 13.8 kJ/mol) from ethane to propane is due to more bulky methyl group.
- Other factors such as **van der Waals attraction or repulsion, dipole-dipole interaction, hydrogen bonding etc.** also affect the stability of conformations.
- But tendency for the bond orbitals on adjacent carbons to be **staggered** remains, and **any rotation away from staggered conformation is accompanied by torsional strain.**

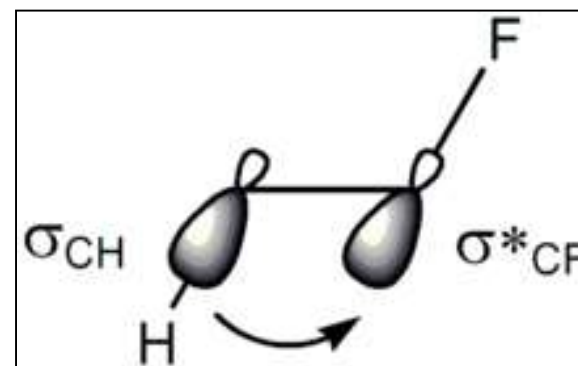
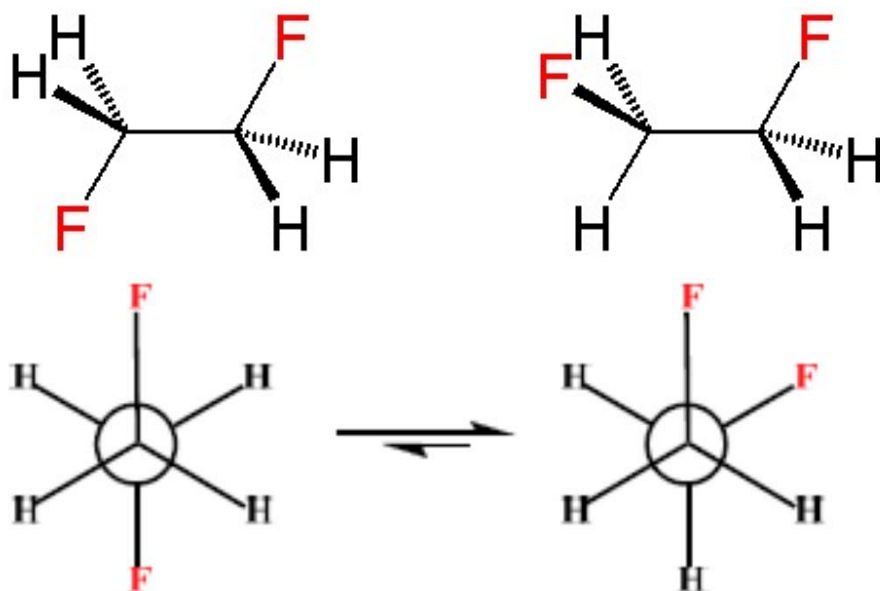


Conformational analysis



The gauche effect: X-C-C-Y containing compounds (where X and Y are electronegative groups) adopt gauche rather than anti conformations – **despite this conformation having a larger overall dipole**. For example, for 1,2-difluoroethane the gauche conformation is more stable by 2.4 to 3.4 kJ/mole in the gas phase.

– Stabilization accrues from $\sigma \rightarrow \sigma^*$ interactions between the best combinations of anti-periplanar donor and acceptor bonds.

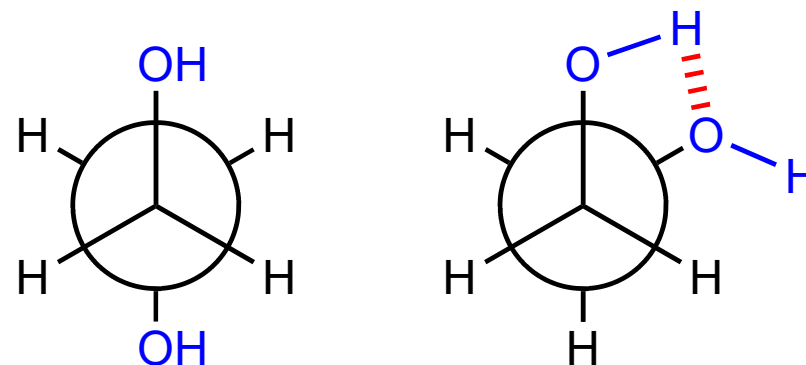


Conformational analysis



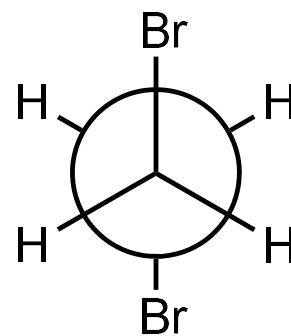
Hydrogen bonding affect

In the case of 1,2-ethanediol an intramolecular H-bond also stabilizes the gauche form.

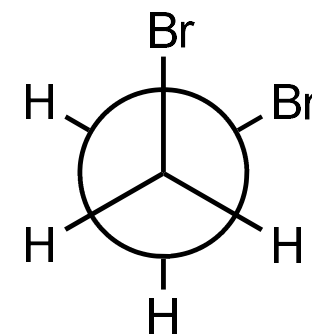


Compounds with the general formula $\text{OHCH}_2\text{CH}_2\text{X}$ are found to be stable in their gauche conformation when $\text{X} = \text{OH}, \text{NH}_2, \text{F}, \text{Cl}, \text{Br}, \text{OR}, \text{NHR}, \text{NR}_2$ etc.

Solvent polarity affect



more stable
in nonpolar solvents



more stable
in polar solvents

What about $\text{NH}_2\text{CH}_2\text{CH}_2\text{CHO}$?