Conformation of Acyclic Molecules

Key Terms:
- **Isomer**: compounds with same molecular formula but different arrangement of atoms
- **Conformational isomers**: same molecular formula and group connectivity but a different spatial arrangement due to the rotation of a single bond (Vollhardt)
    - Can be superposable by bond rotation
- **Dihedral angle**: angle made by 4 atoms covalently attached to each other
- **Barrier to rotation**: energy required to move atom or group past each other
- Types of Strain (Thinkbook)
    - **Strain**: a decrease in molecular stability due to e- repulsion or deviation from ideal geometry
    - **Torsional strain** : strain caused by e- repulsion on one atom or group when passing by another atom or group
        - results from bonds on adjacent atoms being eclipsed
        - brought about by the barrier to rotation
    - **Steric strain** (aka "non-bonding interactions"): strain caused by e- repulsion on an atom or group by another atom or group, which *cannot* be relieved by rotation around a single bond
        - atoms or atom groups repel each other because they are unable to occupy the same location

  **Important Difference: Torsional strain *can* be relieved by bond rotation, but steric strain can *not*

NOTE:
- Ethane has no steric strain → H atoms, even when eclipsed, are not close enough to each other
- For each unfavorable interaction → per pair of eclipsed H-H = 1.0kcal/mol
                                       → per pair of eclipsed CH3-CH3 = 2.5kcal/mol
                                       → per pair of gauche CH3-CH3 = 0.9kcal/mol

Important Concepts:
- Most stable conformation = least van der Waals repulsion
    - → Smaller groups have smaller van der Waals repulsions (e- are further apart)
- Why does bond rotation readily occur around a _-bond?
    - Rotation does not change the degree of orbital overlap
- Why no pi bond rotation?
    - Too energetically expensive → rotation around the _ portion of a pi bond results in a decrease of overlap of adjacent p-orbitals, thereby weakening the pi bond and decreasing stability

How to Determine Relative Amounts of Each Conformation?
- Relative energy difference between conformations tells us something about the relative amounts of each conformation
- Relate Gibbs free energy to equilibrium constant → ΔG = -RTln$K$
    - K = equilibrium constant = ratio of "product" to "reactant"
        - $K > 1$ if right side of equilibrium is favored
        - $K < 1$ if left side of equilibrium is favored
    - R = gas contant (1.987cal/molK)
    - T = temperature in K (usually 298K)

NOTE:
- You will not be required to calculate the values. It is more important that you understand the meaning behind the equation and the magnitude of numbers that it provides.
    - → Magnitude of K allows us to determine the ratio of the two conformations → shows which is more stable and thus favored

How to represent different conformations? Use Newman projections!

(Diagrams source: http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch03/ch3-0-2.html)
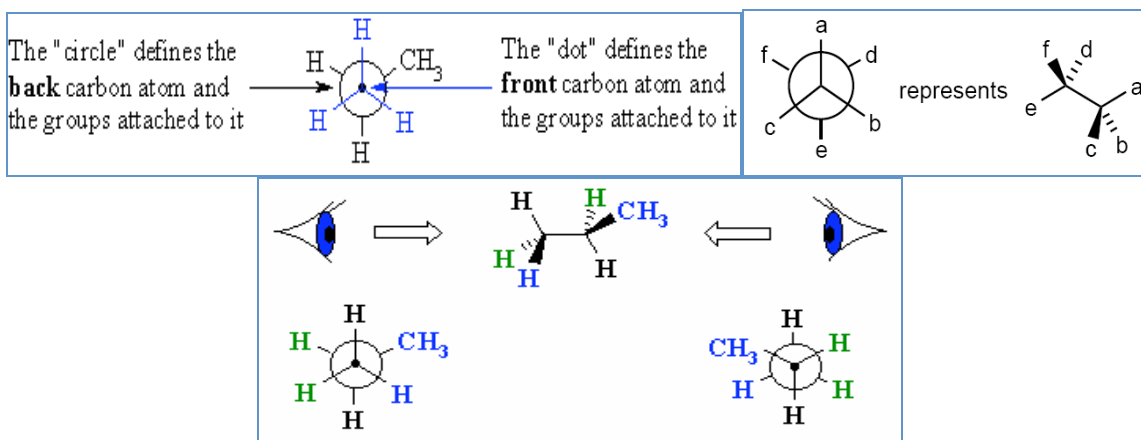
- **Eclipsed** conformation - dihedral angle is 0_
- **Staggered** conformation
  - o **Gauche** – when two largest atoms (or groups of atoms) are staggered adjacent (60_) to each other
  - o **Anti** – when two largest atoms (or groups of atoms) are opposite (180_) each other
    - ▪ most stable because steric hindrance is minimized

Potential Energy Diagram of Rotation About C2-C3 bond in Butane ($CH_3CH_2CH_2CH_3$)
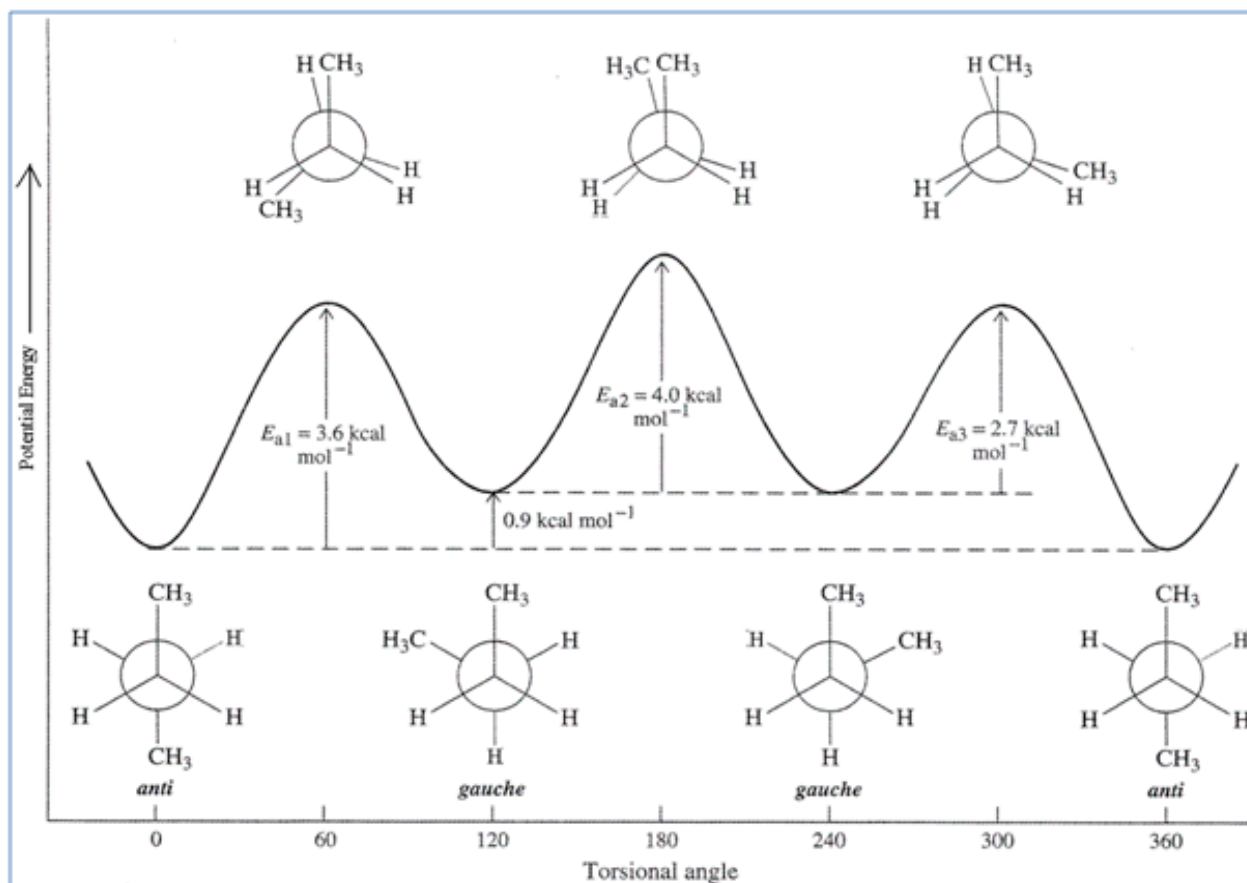
(Diagram source: *Organic Chemistry: Structure and Function* by Vollhardt and Schore, 5th edition, pg 85)