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 cannot

**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 → \( \Delta G = -RT\ln K \)
  - \( K = \) 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 constant (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!
• **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 (\(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\))