

Molecular Flexibility: Acyclic Molecules

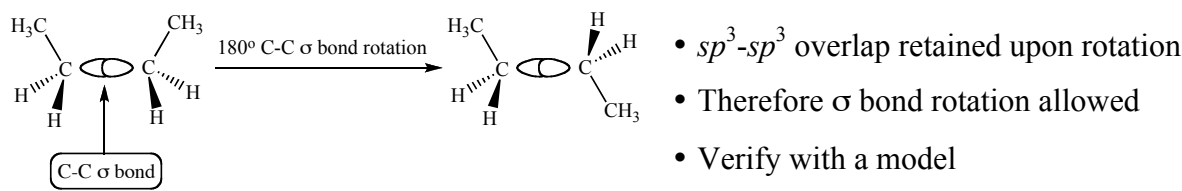
Bond Rotation

Molecular structure is usually not static: Bonds vibrate
Bonds rotate

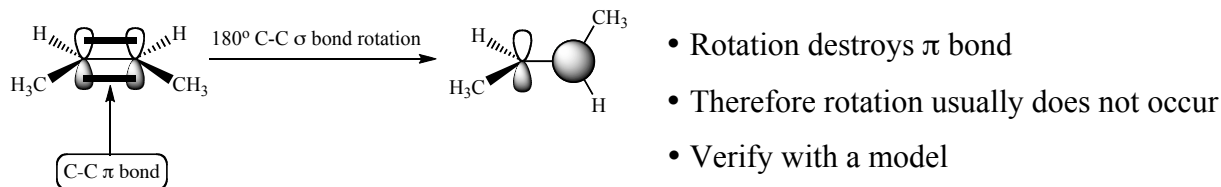
Bond stability proportional to orbital overlap

- Therefore bond rotation allowed *as long as orbital overlap not disrupted*

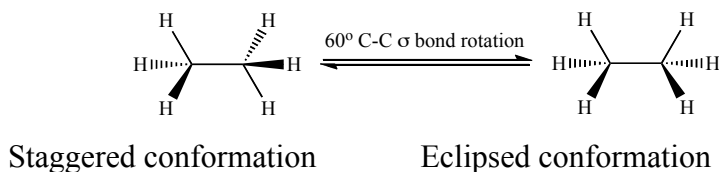
Example: $C_{sp^3}-C_{sp^3}$ σ bond of ethane (H_3C-CH_3)



Example: $C_{sp^2}-C_{sp^2}$ σ and π bonds of ethylene ($H_2C=CH_2$)

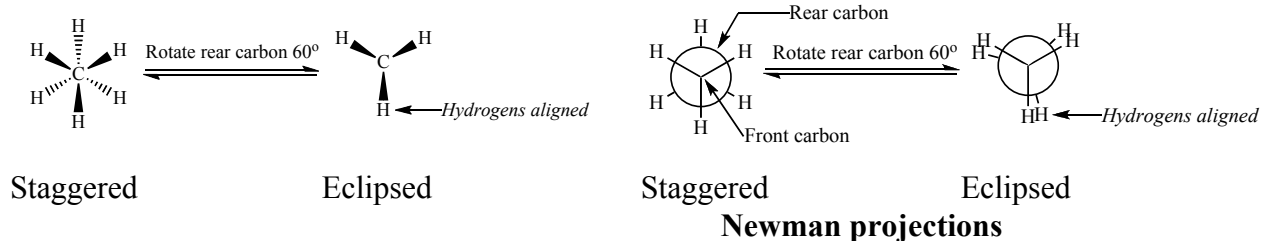


Ethane: The Simplest Case



Conformational isomers (conformers): Isomers that can be interconverted by rotation around one or more single bonds.

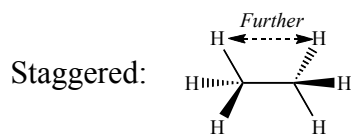
View of ethane along the carbon-carbon bond axis:



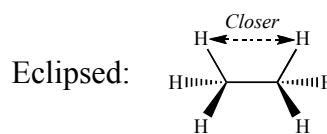
Compare Newman projections with models.

Question: Ethane has an infinite number of conformations. Which is the best representation of ethane?

Answer: Structure with the lowest potential energy



Electron domains further apart*
Less electron repulsion
More stable conformation**

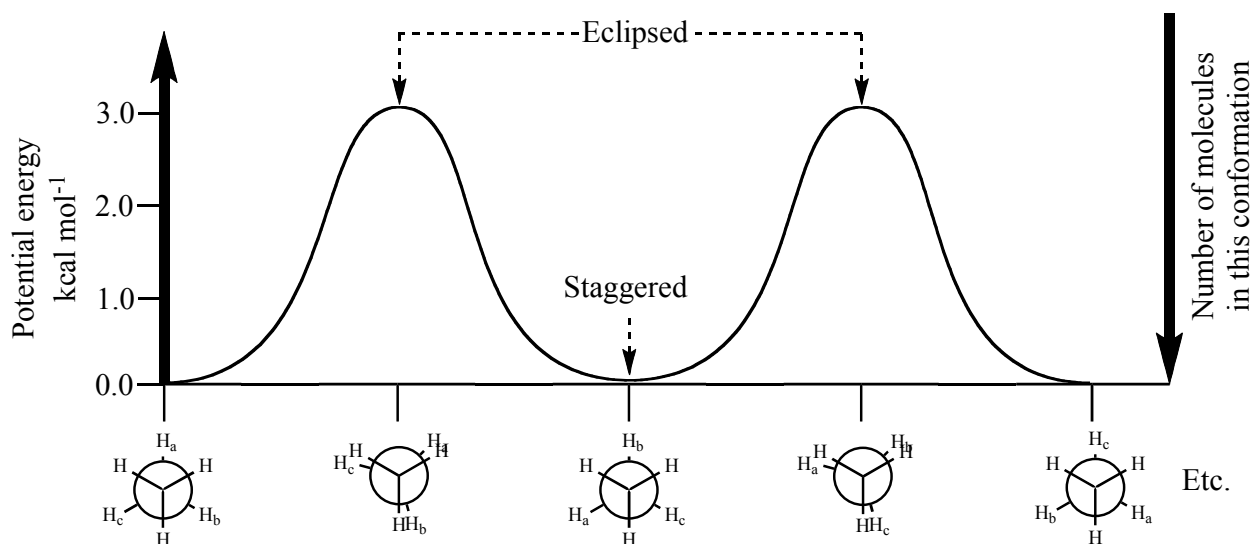


Electron domains closer*
More electron repulsion
Less stable conformation

* Verify with models

** Major ethane conformation, but not solely populated

Energy versus conformation:



Strain: An increase in potential energy due to a deviation from ideal molecular geometry.

- Ethane strain caused by electron repulsion
- Potential energy (eclipsed) - potential energy (staggered) = $3.0 \text{ kcal mol}^{-1}$ strain in ethane

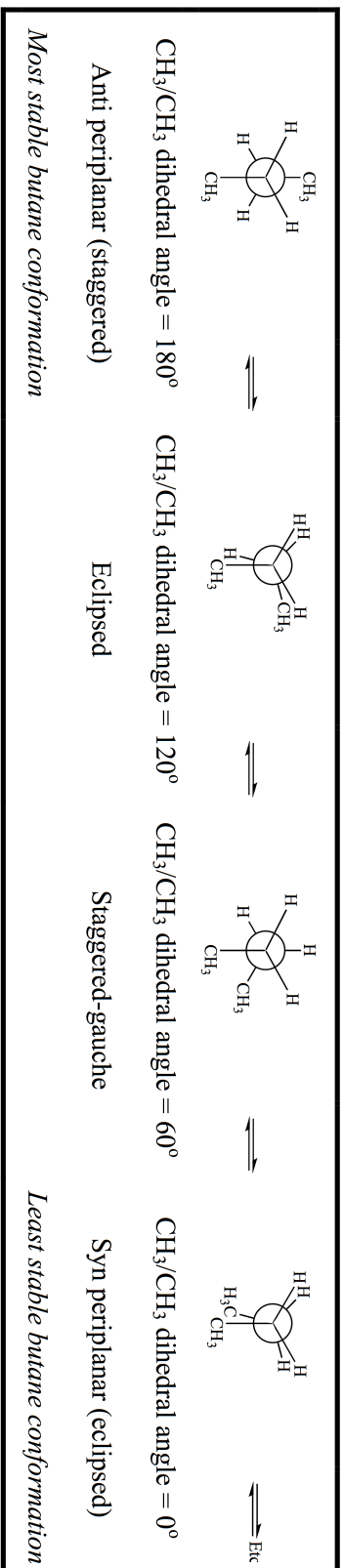
Torsional strain: Strain that can be reduced by rotating around one or more single bonds.

- Eclipsed - staggered = 3 H/H eclipsing interactions
= $3.0 \text{ kcal mol}^{-1}$
One H/H eclipsing interaction = $1.0 \text{ kcal mol}^{-1}$

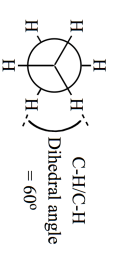
Barrier to rotation: Difference in energy between most stable and least stable conformations.

- Despite barrier of $3.0 \text{ kcal mol}^{-1}$, rapid C-C bond rotation ($\sim 10^{11}$ rotation cycles s^{-1})
- Ethane spends $\sim 99\%$ of time in staggered conformation
- Ethane properties derived from weighted average of conformations, but mostly staggered

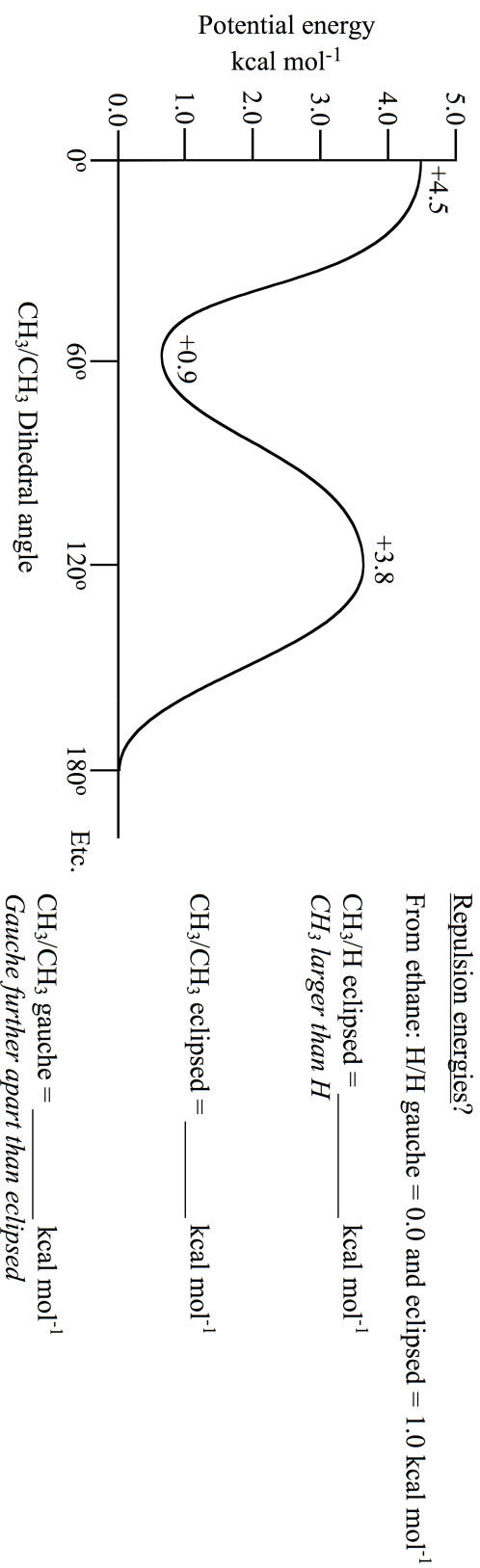
What Happens When Electron Domains Are Unequal? Conformational Isomers of Butane



Dihedral angle: Angle between two planes defined by three atoms each. Usually the angle between two bonds.



Gauche: Conformation or groups with a dihedral angle of 60°.



Repulsion energies?

From ethane: H/H gauche = 0.0 and eclipsed = 1.0 kcal mol⁻¹

CH₃/H eclipsed = _____ kcal mol⁻¹

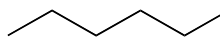
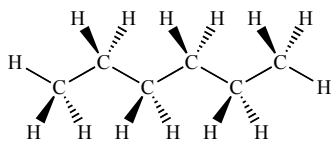
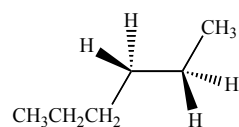
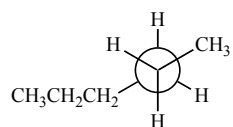
CH₃ larger than H

CH₃/CH₃ eclipsed = _____ kcal mol⁻¹

CH₃/CH₃ gauche = _____ kcal mol⁻¹

Gauche further apart than eclipsed

Preference for anti-staggered conformations → elongated “W” shape for alkanes



Verify with molecular model of hexane