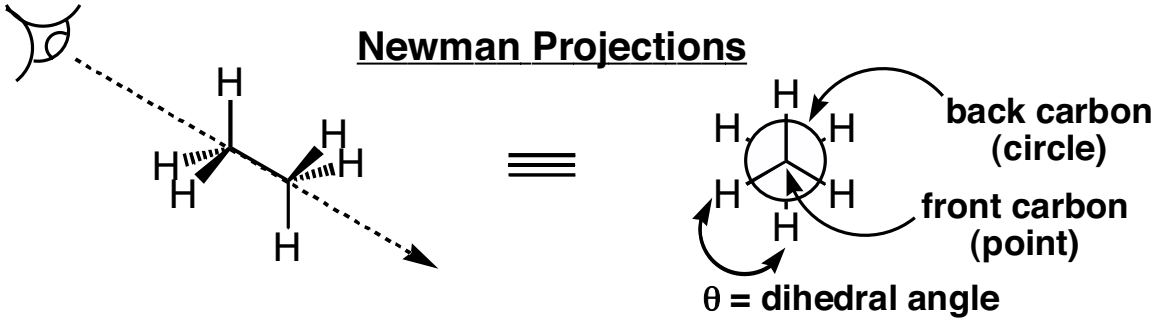
Conformational Analysis: The Fundamentals

conformational analysis: study of the energetics of different conformations

conformations: structures related by bond rotations; usually interconvertible at RT

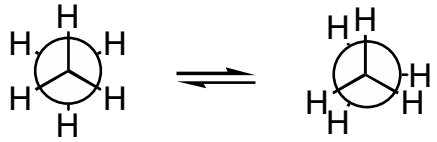
conformer: conformation at potential energy minima

Newman Projections



Barrier to Rotation: torsional energy; energy required to twist a bond into a specific conformation;
Barrier to Rotation = E_{rel} (highest energy conformer) – E_{rel} (lowest energy conformer)

Ethane



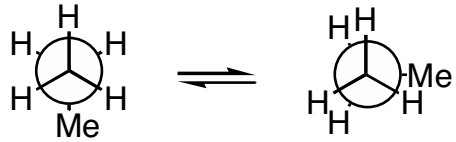
staggered
θ = 60°
E_{rel} = 0 kcal/mol

eclipsed
θ = 0°
E_{rel} = 3.0 kcal/mol

Barrier to Rotation = 3.0 – 0 = 3.0 kcal/mol

H/H-eclipsing = 1.0 kcal/mol

Propane



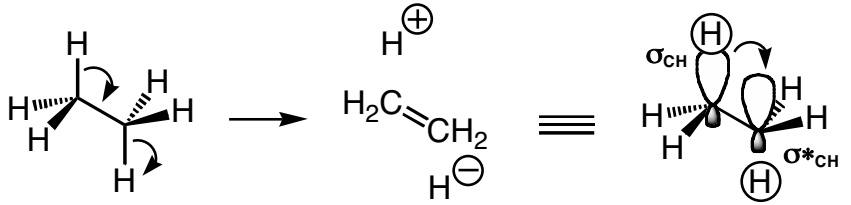
staggered
θ = 60°
E_{rel} = 0 kcal/mol

eclipsed
θ = 0°
E_{rel} = 1.4 kcal/mol

Barrier to Rotation = 1.4 – 0 = 1.4 kcal/mol

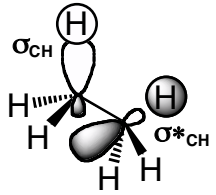
H/Me-eclipsing = 1.4 kcal/mol

• One explanation for the lower energy of staggered ethane is that **the staggered conformer is stabilized by hyperconjugation** (stabilizing overlap between σ_{CH} and σ^*_{CH} orbitals that does not occur in the eclipsed conformer).



Hyperconjugation (staggered)

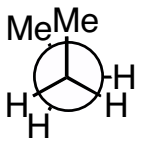
(good overlap)



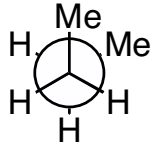
eclipsed (poor overlap)

• The barrier to rotation for propane is slightly higher than ethane because there is electron repulsion between the methyl group and the eclipsed hydrogen atom in the eclipsed conformer.

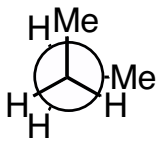
Butane



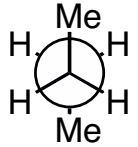
fully eclipsed
(eclipsed)
$\theta_{Me/Me}$ = 0°
E_{rel} = 4.6 kcal/mol



gauche
(staggered)
$\theta_{Me/Me}$ = 60°
E_{rel} = 0.9 kcal/mol



eclipsed
(eclipsed)
$\theta_{Me/Me}$ = 120°
E_{rel} = 3.8 kcal/mol



anti
(staggered)
$\theta_{Me/Me}$ = 180°
E_{rel} = 0 kcal/mol

Barrier to Rotation = 4.6 – 0 = 4.6 kcal/mol

→ **Me/Me-eclipsing = 2.6 kcal/mol***

→ **Gauche Butane Interaction (gbi) = 0.9 kcal/mol**

Numbers to Remember

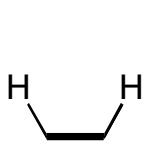
H/H-eclipsing = 1.0 kcal/mol

H/Me-eclipsing = 1.4 kcal/mol

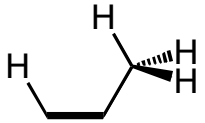
Me/Me-eclipsing = 2.6 kcal/mol*

Gauche Butane (gbi) = 0.9 kcal/mol

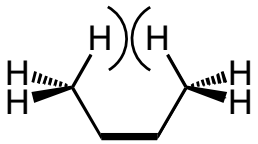
The Me/Me-eclipsing interaction is said to be worth various values in other sources. A Me/Me-eclipsing interaction is significantly higher than an H/H- or H/Me-eclipsing interaction because the hydrogens on the two methyl groups can actually bump into each other (steric strain).



H/H



H/Me



Me/Me