Chapter 6 Stereochemistry I

- What to master
  - Recognizing Cis-Trans Isomers and Estimating Their Relative Stabilities
  - Designating the Configuration of Cis-Trans Isomers
  - Determining Conformations about Single Bonds and Estimating Their Relative Energies
  - Understanding the Types and Relative Amounts of Strain in Cyclic Molecules
  - Determining the Relative Stabilities of Conformations of Cyclohexane Derivatives

Chapter 6 Stereochemistry I

"3-D structure of (organic) molecules"

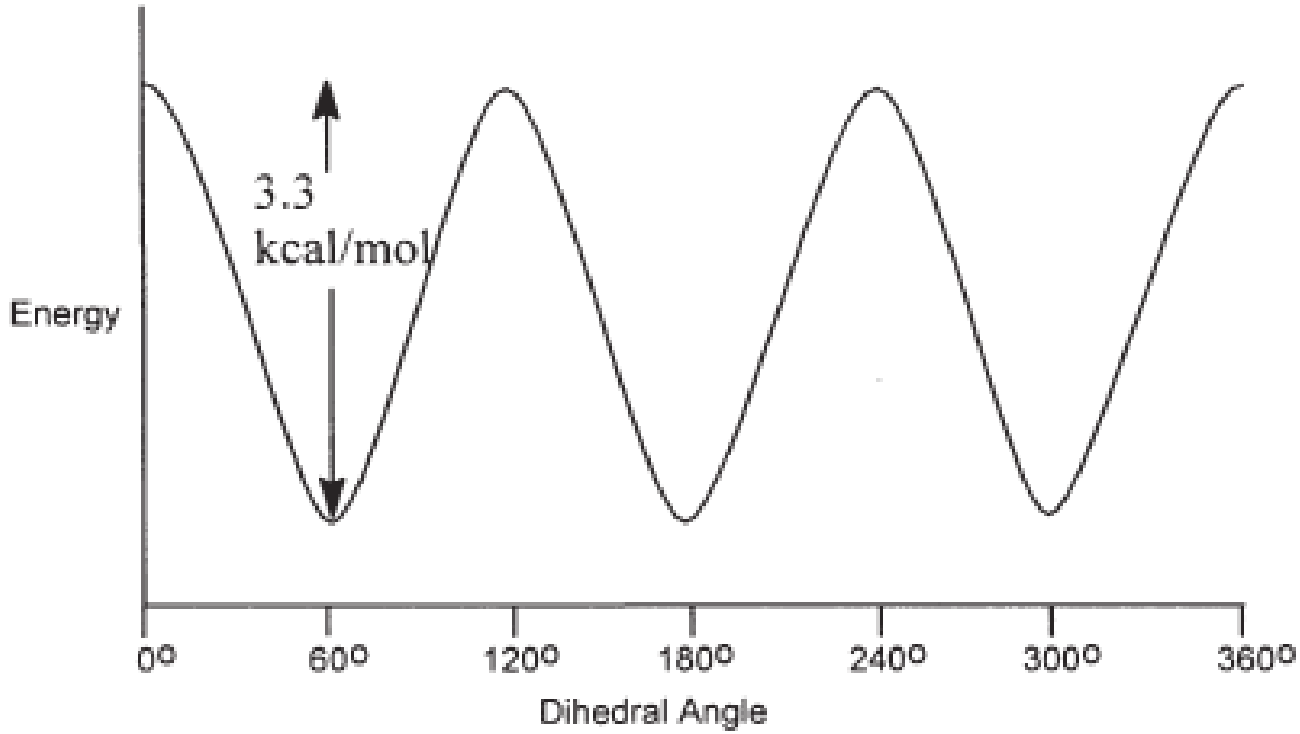
- Isomers: different molecules with the same MF
  - structural (constitutional) isomers: different connectivity
  - stereoisomers: different spatial arrangement
    - cis-trans isomers: 2-butene; 📖 179 middle
    - restricted rotation about the double bond: 📖 180 Figure 6.1
    - stereocenter (stereogenic atom): 📖 180 bottom
  - *practice*: 📖 181 Problem 6.1

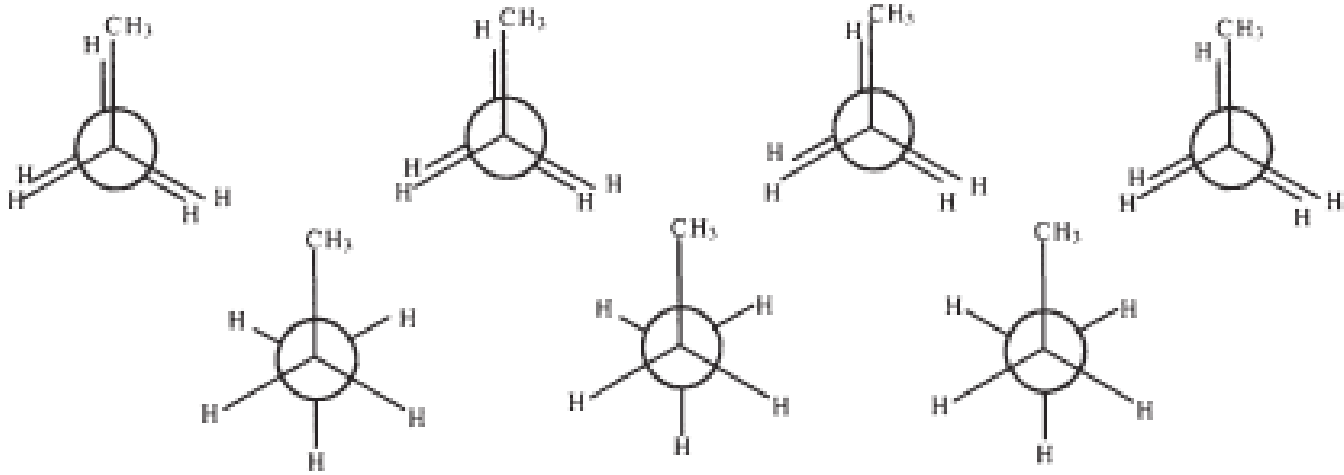
❖ Cis-Trans Isomers

- Relative stability of alkenes: 2-butene
  - heat of (catalytic) hydrogenation: 📖 181 Figure 6.2
  - steric hindrance (crowding/strain): 📖 182 Figure 6.3
- Configuration of cis-trans isomers: *Z* & *E* (*cis* & *trans*)
  - 3-D arrangement of groups about a stereocenter
  - Cahn-Ingold-Prelog sequence rules: priority; 📖 183 bottom
    - higher atomic number up to the first point of difference
    - multiple atoms for multiple bonds: 📖 184-5
  - *practice*: 📖 185 Practice 6.1 & 📖 186 Problem 6.4

❖ Conformations

- Definition: spatial arrangements around single bonds
  - eclipsed & staggered conformers: ethane, 📖 188 Figure 6.4
    - torsional (rotational) strain: ΔE = 2.9 kcal/mol; 📖 188 Figure 6.5
    - neither isolable nor separable at RT: free rotation
  - conformational analysis: torsional strain vs dihedral angle
    - propane: ΔE = 3.3 kcal/mol; 📖 189 middle & *Problem 6.5*
    - butane: C2-C3; 📖 190 Figure 6.6 & 197 Figure 6.7
  - the 'zigzag' conformation: most stable; 📖 193 middle
  - *practice*: 📖 192 Practice 6.2 & 📖 193 Problem 6.6


3.3
kcal/mol
Energy
0°
60°
120°
180°
240°
300°
360°
Dihedral Angle



❖ Conformations of Cyclic Molecules

- less flexible & more strained than acyclic molecules
  - strain energy of cycloalkanes: 📖 194 Table 6.1
    - origins of the strain: length, angle, torsional, non-bonded
  - cyclopropane: planar; 📖 195 Figure 6.8 (angle & torsional)
  - cyclobutane: butterfly; 📖 196 Figure 6.9 (angle & torsional)
  - cyclopentane: envelope/half-chair; 📖 196 Figure 6.10 (much less strained)

❖ Conformations of Cyclohexane

- Nearly strain-free chair conformation: 📖 197 Fig. 6.11
  - axial / equatorial substituents: up / down; 📖 197 Figure 6.11
  - how to draw the chair conformation: 📖 199 Figure 6.13
  - boat/twist boat conformations: more strained; 📖 198 Fig. 6.12
- Ring-flipping of cyclohexane: 📖 200 Figure 6.14
  - chair ⇌ half-chair ⇌ twist-boat ⇌ boat
  - energy diagram of the ring-flipping process: 📖 200 Fig. 6.15

Conformations of Other Rings

- Cycloheptanes: similar strain to cyclopentanes
  - twist chair ≤ chair < twist boat ≤ boat: mostly torsional strain
- Medium-sized rings: 8~11-membered rings
  - rather strained: transannular strain, ca. 4~9 kcal/mol higher
- Commonly found rings: 3-, 5-, 6-, & 7-rings
- Benzene rings: no strain; sp^2 (120^o, planar)

Cyclohexanes with One Substituent

- Methylcyclohexane: 📖 203 Figure 6.16
  - 1,3-diaxial interactions: 1.7 kcal/mol
    - conformer ratio at 25 °C: $K = e^{-(-1700)/(1.987 \times 298)} \cong 18$ [$\Delta G^o = -RT \ln K$]; equatorial:axial = 95:5, 📖 204 Practice 6.3
  - axial strain energy: conformational free energy ('A value'); 📖 204 Table 6.2
    - isopropyl vs *tert*-butyl: 📖 205 top
  - *practice*: 📖 205 Problems 6.8 & 6.9

Cyclohexane with Two or More Substituents

- dimethylcyclohexanes: cis-trans stereoisomers
  - 1,2-dimethylcyclohexane: *cis*- & *trans*-isomer; 📖 208 bottom
    - conformers: *cis*; 📖 210 Figure 6.17, *trans*; 📖 211 Figure 6.18
    - $\Delta E \cong$ 2.5 (*cis*) - 0.8 (*trans*, diequatorial) $\cong$ 1.7 kcal/mol
  - 1,3-dimethylcyclohexanes: $A_{\text{(Me-Me 1,3-diaxial)}}$; 📖 211 bottom
    - *practice*: 📖 212 Problem 6.12
  - cyclohexane with different substituents: 📖 218
    - 1-methyl-4-phenylcyclohexane: *cis*-isomer vs *trans*-isomer
    - *practice*: 📖 213 Problems 6.13 & 6.14

공부하는 방법

"그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이, 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다.

이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다." - 퇴계 이황 (금장태 著)