Molecular Conformations [Daley & Daley ch 3]

This presentation of the material covered within a topic or chapter is meant to give students a clear vision of the central concepts or big picture concepts that all other information expands upon, relates to or serves.
Super concepts are the big picture, central concepts that should be completely obvious to you as we begin to cover them and when you reflect on the topic once we've covered it. Everyone who takes the course should be able to remember or recognize the super concepts years after having taken the course.
Each concept is an important "chunk" of a super concept. Each concept is a large enough idea to stand on its own. Good (B) students will remember and understand these concepts after taking the course.
The details are ideas, methods, or facts that you need to understand to solve problems and actually do chemistry. It's likely that only the best (A) students will be able to remember and use the details years after taking the course.

Superconcepts:

1. Most molecules are flexible and can adopt a variety of conformations.
2. Molecules tend to seek and remain in their lowest energy conformations.

Concepts:

a. Conformation = the 3D shape of a molecule
b. Alkanes rotate through conformations known as conformers or rotamers like staggered and eclipsed.
c. If molecular conformers are plotted vs. energy, staggered conformations are seen at energy minima while eclipsed conformations are seen at energy maxima.
d. Steric hindrance is 3D crowding or interference by adjacent atoms or functional groups. Large substitutents or functional groups like butyl groups are more likely to sterically hinder their neighbors than hydrogen atoms. Tert-butyl groups (1,1-dimethylethyl) are famously bulky and exert significant steric hinderance.
e. With the exception of cyclopropane, cycloalkane rings are not planar but puckered in order to maintain bond angles as close as possible to 109.5° bond angles for carbons with four substitutents.
f. Rings may have cis and trans stereoisomers. Generally, the isomer that places large substituents in the equatorial position is the most stable.

Details:

i. Molecular conformation can effect the physical, chemical & biological properties of molecules.
ii. Alkanes rotate spontaneously through staggered & eclipsed conformations.
iii. Little energy is required for rotation around single bonds.
iv. The staggered conformation is more stable (lower energy) than the eclipsed conformation; staggered is favored more than 90:10.

v. Conformers (or rotamers) can be represented by dash-wedge, sawhorse or Newman projection diagrams.
vi. Torsion angles (aka dihedral angles) are angles of rotation between adjacent substituents in molecular conformations.
vii. Gauche refers to groups separated by 60° torsion angles.
viii. Anti refers to groups separated by 180 degree torsion angles.
ix. If a molecule includes two large substituents then the staggered conformation in which the two are anti is more stable than the conformation in which they are gauche. Likewise, the least stable eclipsed conformation occurs when the two large groups are directly eclipsed in front of and behind each other.
x. Cyclohexane puckers into either chair or boat forms. The chair form is more stable because chair hydrogens are staggered while boat hydrogens are eclipsed and because the chair gives each substituent (particularly flagpole substituents) maximal space.
xi. In the chair form of cyclohexane, each carbon has both axial and equatorial substituents. Axial positions are directly above and below the average plane of the ring. Equatorial positions surround the ring and give substituents more space and thus less steric hindrance.
xii. Flipping cyclohexane chairs causes all axials to become equatorial and vv.
xiii. Ring stability is maximized when large substituents are placed in equatorial positions.