Chapter 3 - Organic Compounds: Alkanes and Cycloalkanes

Cycloalkanes

All single bonds freely rotate at room temperature (and even much lower). Thus, linear alkanes are constantly spinning and twisting. By tying the two ends into a ring, this prohibits free rotation around the single bonds and this makes cycloalkanes much less flexible.

Stereoisomers: Isomers (different compounds) that have all the same number and kind of atoms that are all connected the same, but differ in their arrangement in three dimensions.

Because of the restricted rotation in cycloalkanes, substituents could either be on the same side (cis) or opposite sides (trans) of the plane of the ring. These are only different in their three dimensional arrangement of the substituents.

Chapter 4 - Stereochemistry of Alkanes and Cycloalkanes

Conformations of Alkanes

As stated above, all single bonds freely rotate at room temperature (unless constrained by a ring). Thus, linear alkanes are in constant motion. If the molecule were frozen to absolute zero you could see different arrangements of the groups depending on the state of the bond rotations.

Conformers: Different rotational isomers (conformations) of a molecule. They are rapidly changing.

Conformations of Ethane, Propane and Butane

Some definitions will be useful to discuss the conformations of alkanes.

Newman Projection: A view of a molecule looking straight done one C-C single bond (see below)

Sawhorse Projection: A view of a molecule showing wedges and dashes for coming out or into the plane of the paper - resembles a sawhorse (see below)
Staggered: Relationship between groups on one carbon versus an adjacent carbon (front and back on a Newman projection). A staggered conformation is one in which the groups on the front are 60° out of alignment from the groups on the back (exactly in between as far apart as possible).

Eclipsed: Relationship between groups on one carbon versus an adjacent carbon (front and back on a Newman projection). An eclipsed conformation is one in which the groups on the front are aligned exactly with the bonds on the back carbon (as close as possible).

Torsional Strain: The strain introduced by electron repulsions on bonds of adjacent carbons. This is highest when the bonds are eclipsed with one another. This causes the eclipsed conformation of alkanes to be higher in energy than staggered conformations.

Steric Strain: The strain introduced when atoms are forced to become close to each other (they bump into each other). This increases as the size of groups increases.

Anti Conformation: In butane, the anti conformation is the one in which the two methyl groups on adjacent carbons are as far apart as possible (180°) in a staggered conformation (see below).

Gauche Conformation: A gauche relationship in butane is the one in which the two methyl groups on adjacent carbons are still staggered, but closer (60° apart) (see below).

If you were to map the energy level of ethane as the front carbon rotates around 360° relative to the back carbon, you would see a graph like this.

The energy map for propane would look identical to that of ethan however the added size of the methyl group (instead of H) would add a little bit of steric strain to the conformations. Thus, the eclipsed conformation for propane would be 3.4 kcal/mol higher than than the staggered.
If you examine the different conformations of butane (looking down the C2-C3 bond), you will find that as you go around 180° there are different interactions between the methyl groups. Thus, there are different staggered and different eclipsed conformations.

The ANTI conformation is the most stable conformation. See the sawhorse and Newman projections for this conformation and compare them to the sawhorse and Newman views on the models below.

If you rotate the anti conformer 60° you will find an eclipsed conformation that has both methyls (front and back) adjacent to Hydrogens. This is 3.8 kcal/mol higher in energy than the anti-staggered conformation.
If you rotate another 60° you will get to another staggered conformation that has the methyl groups only 60° apart. This is the gauche butane conformation.

Butane Conformations

The eclipsed conformation with both methyl groups bumping into each other is the highest energy conformation being 4.5 kcal/mol higher than the anti-staggered conformation.

Butane Conformations

Below is the energy diagram for a 360° rotation of butane starting with the lowest energy staggered anti conformation.