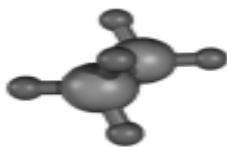


Rotation in Substituted Ethanes

Rotation in substituted ethanes is an example of general rotation about single, sigma, carbon-carbon bonds. The different conformations resulting from these single bond rotations are energetically very similar, making such rotations both common and important in understanding how alkanes act. Often a particular conformation of the molecule is required for a reaction to proceed, and can explain the product stereochemistry, so understanding how to visualize the different forms and how they interconvert is essential to understanding complicated reaction mechanisms.

Introduction

While the carbon-carbon single bonds of ethane must adhere to certain physical limitations (both carbons are sp^3 hybridized, all bond angles are approximately 109.5° , etc), these criteria still allow a lot movement within the molecule. With a small amount of activation energy, substituents are free to rotate around the bond, like the blades on a fan rotate about the hub.



The most common and simplest way of depicting rotations about substituted ethanes is a Newman Projection. This simplifies the molecule into a 2-D sketch that can readily show the differences between conformations. (A conformation is a particular arrangement of the substituents of one carbon in a bond, with respect to the substituents of the other carbon in the bond)

There are two different classifications for the conformations:

Staggered - the substituents, as drawn in the Newman Projection, all have 60 degrees between them. These conformers are always the lowest points in relative energy diagrams.

- **anti** conformations are the lowest possible energy conformations; all substituents have a maximum amount of free space.
- **gauche** conformations are higher energy than anti conformations, but lower energy than any eclipsed forms. This is due to proximity of the substituents. In the gauche conformation, unlike any eclipsed forms, the substituents are not directly aligned. However, they are close enough to influence each other and raise the energy of the molecule.

(See attached "Energy Diagram" for relative energies of Newman Projections of the C3-C4 bond in 3,4-dimethylhexane)

Eclipsed - the substituents are overlapping, when viewed as in the Newman projection. With a model kit, this is the form where all the substituents are aligned and the ones on the carbon farthest from your eyes are hidden behind the substituents of the foremost carbon. Depending on which groups are overlapping, eclipsed forms can have varying energies. They do not have specific names, like anti vs gauche. The eclipsed conformer with the largest group on each carbon overlapping with each other will always be the highest energy conformer of that bond.

To convert between eclipsed and staggered conformations (or vice versa), one carbon, with all of its substituents, is rotated 60 degrees. You can imagine the projection like a combination lock. The back carbon is like the lock itself and the front carbon like the knob you turn to enter your combination. "grasp" the front carbon, and turn in 60 degrees. The placement of the back substituents will not change. (In reality, all the substituents are rotating simultaneously.) Repeating this process 6 times will produce all staggered and eclipsed conformations of the bond in question, and bring you back to the conformation you began with.

Any conformations between eclipsed and staggered are called skew conformations, but as there are an infinite number of these for each bond, (depending on how much or little the bond is rotated) skew conformations are rarely represented. (See attached "Newman Projections" to view Newman Projections of 3,4-dimethylhexane)

Unsubstituted Ethane: Only has two conformers! Because all the substituents are exactly the same (all hydrogens), there is only one eclipsed and one anti conformation, each. The eclipsed formation is 3 kcal/mol higher in energy - 1 kcal/mol for each eclipsed hydrogen.

Substituted Ethane: Substituted ethanes have slightly greater differences in energy between conformations because of steric hindrance. Essentially, the larger groups bump up against each other during the transition state, so it takes more energy to move them around each other. The large substituents are like beach balls that knock into each other while moving around, as opposed to hydrogens, which are smaller, and more compact (imagine trying to move two volleyballs past each other in a 16 inch box, versus two golf balls in the same volume). This hindrance raises the energy of all conformations of the molecule (when compared to unsubstituted ethane, or less-substituted bonds).

(See bottom of attached "Newman Projections" for Ethane Conformations)

Source: http://chemwiki.ucdavis.edu/Organic_Chemistry/Fundamentals/Rotation_in_Substituted_Ethanes