

4.3: STRUCTURE AND CONFORMATIONS OF ALKANES

Learning Objective

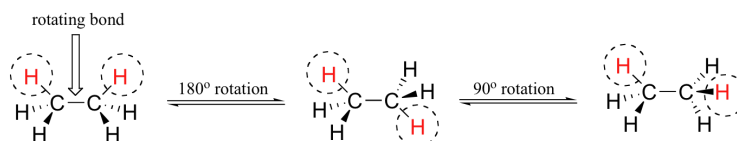
- interpret and draw the rotation about a carbon-carbon single bond using Newman projections and sawhorse structures
- correlate energies of conformations with rotational energy diagrams

Single Bond Rotation and Conformational Isomerism

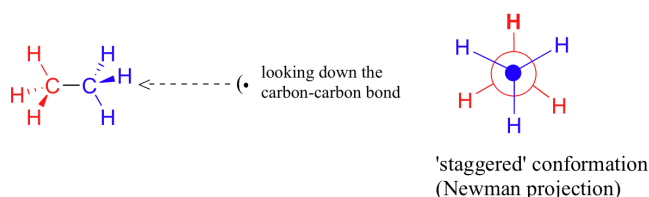
Conformational isomerism involves rotation about sigma bonds, and does not involve any differences in the connectivity or geometry of bonding. Two or more structures that are categorized as conformational isomers, or **conformers**, are really just two of the exact same molecule that differ only in terms of the angle about one or more sigma bonds. The carbon-carbon single bonds of alkanes rotate freely. Conformers are the same molecule shown with different sigma bond rotations. Newman projections are one way to communicate bond rotation.

ETHANE CONFORMATIONS

Although there are seven sigma bonds in the ethane molecule, rotation about the six carbon-hydrogen bonds does not result in any change in the shape of the molecule because the hydrogen atoms are essentially spherical. Rotation about the carbon-carbon bond, however, results in many different possible molecular conformations.



In order to better visualize these different conformations, it is convenient to use a drawing convention called the **Newman projection**. In a Newman projection, we look lengthwise down a specific bond of interest – in this case, the carbon-carbon bond in ethane. When there are multiple carbons, then we specify the bond of interest using the carbon numbers from the IUPAC name. We depict the ‘front’ atom as a dot, and the ‘back’ atom as a larger circle.



The six carbon-hydrogen bonds are shown as solid lines protruding from the two carbons at 120° angles, which is what the actual tetrahedral geometry looks like when viewed from this perspective and flattened into two dimensions.

The lowest energy conformation of ethane, shown in the figure above, is called the ‘staggered’ or ‘anti’ conformation, in which all of the C-H bonds on the front carbon are positioned at dihedral angles of 60° relative to the C-H bonds on the back carbon. In this conformation, the distance between the bonds (and the electrons in them) is maximized.

If we now rotate the front CH₃ group 60° clockwise, the molecule is in the highest energy ‘eclipsed’ conformation, where the hydrogens on the front carbon are as close as possible to the hydrogens on the back carbon.



This is the highest energy conformation because of unfavorable interactions between the electrons in the front and back C-H bonds. The energy of the eclipsed conformation is approximately 3 kcal/mol higher than that of the staggered conformation.

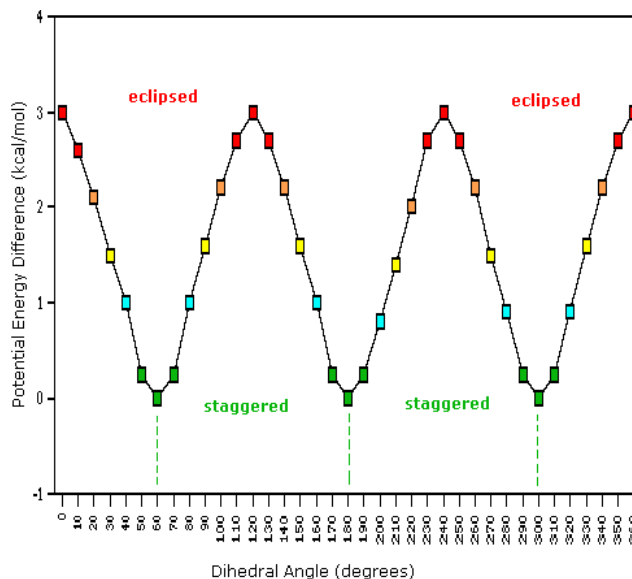
Another 60° rotation returns the molecule to a second eclipsed conformation. This process can be continued all around the 360° circle, with three possible eclipsed conformations and three staggered conformations, in addition to an infinite number of variations in between.

The carbon-carbon bond is not *completely* free to rotate – there is indeed a small, 3 kcal/mol barrier to rotation that must be overcome for the bond to rotate from one staggered conformation to another. This rotational barrier is not high enough to prevent constant rotation except

at extremely cold temperatures. However, at any given moment the molecule is more likely to be in a staggered conformation - one of the rotational 'energy valleys' - than in any other state.

FREE ROTATIONS DO NOT EXIST IN ETHANE

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Although the conformers of ethane are in rapid equilibrium with each other, the 3 kcal/mol energy difference leads to a substantial preponderance of staggered conformers (> 99.9%) at any given time. The animation below illustrates the relationship between ethane's potential energy and its dihedral angle

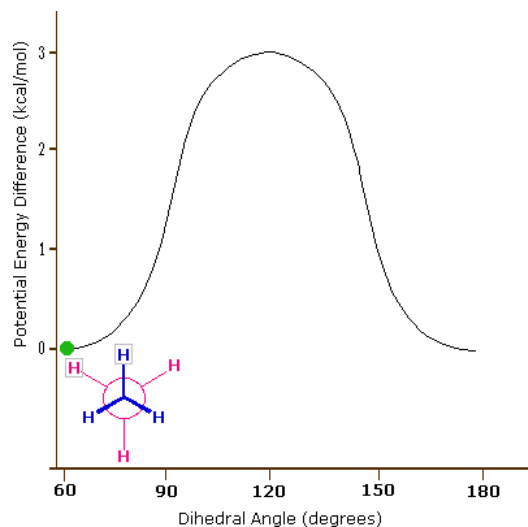


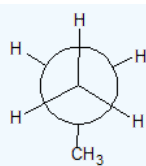
Figure 3.6.X: Animation of potential energy vs. dihedral angle in ethane

Exercise

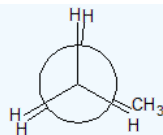
1. Draw the Newman projections for the staggered and eclipsed conformers of propane along the C1-C2 axis.

Answer

- 1.



staggered



eclipsed

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