

Strain

Definition: Strain is defined as the distortion of bond lengths and bond angles from their ideal values.

What does that mean? When a bond length or bond angle is distorted, potential energy is stored in the molecule. This potential energy that is stored in the molecule is referred to as the **strain** or the **strain energy**. Alternatively, strain can be thought about as the distortion of a molecule due to the atom's three dimensional bonding requirements. Broadly speaking, there are three classes of strain.

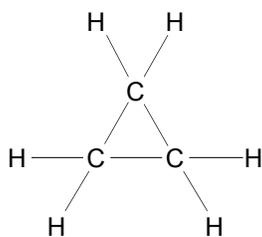
Classes of Strain:

1. **Angle Strain**
2. **Steric Strain**
3. **Torsional Strain**

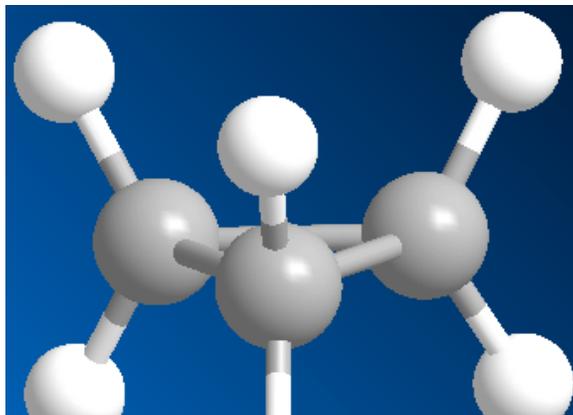
Angle Strain: Angle strain is the potential energy stored in a molecule due to the displacement of the bond angles from their equilibrium values. The equilibrium values are 109.5° for sp^3 hybridized atoms, 120° for sp^2 hybridized atoms, and 180° for sp hybridized atoms. Let's review a few examples that show angle strain.

Example: Cyclopropane

The Lewis structure of cyclopropane is shown below.



The three dimensional structure of cyclopropane is shown



structure of below.

The bond angles in cyclopropane are 60° , as cyclopropane is in the shape of an equilateral triangle. Because each carbon atom is sp^3 hybridized, one would expect the ideal bond angle values to be 109.5° . We can see that there is a large discrepancy between the actual bond angles (60°) and the ideal bond angles (109.5°). This large discrepancy results in a large amount of angle strain and increases the potential energy stored in the molecule. Furthermore, the hydrogens of cyclopropane are eclipsed, resulting in additional strain due to steric repulsions (see section on steric repulsions). As a side note, the bonding in cyclopropane is the result of poor orbital overlap amongst the carbons. Some scientists have termed this poor orbital overlap “banana bonds”.¹

Consequences of Angle Strain: The angle strain of cyclopropane renders the molecule unstable and highly reactive due to the large amount of potential energy stored in the molecule. Cyclopropane, when burned, releases substantially more energy than when propane is burned.² This difference cannot be explained solely by the fact that there are two additional hydrogens in propane. The higher heat of combustion of cyclopropane is due to the angle strain. It is known that cyclohexane does not undergo hydrogenation reactions. However, cyclopropane does readily undergo hydrogenation reactions.² This difference in reactivity is due to the high potential energy stored in cyclopropane, whereas there is little potential energy in cyclohexane.

The second type of strain commonly found in molecules is called steric strain.

Steric Strain: Steric strain results from the electron-electron repulsion of atoms (or groups of atoms) that are too close together. Steric strain stores potential energy in a molecule by forcing repelling groups together. An example of a molecule that exerts steric strain is discussed below.

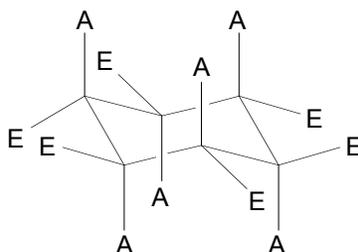
Example: 1, 3-diaxial repulsions of cyclohexane

Cyclohexane in its chair conformation has equatorial and axial positions. In substituted cyclohexanes, such as methylcyclohexane, the substituent will encounter steric repulsions when it is in the axial position. These steric repulsions are termed “1,3-diaxial repulsions” because they involve axially oriented groups in the 1 and 3 positions.

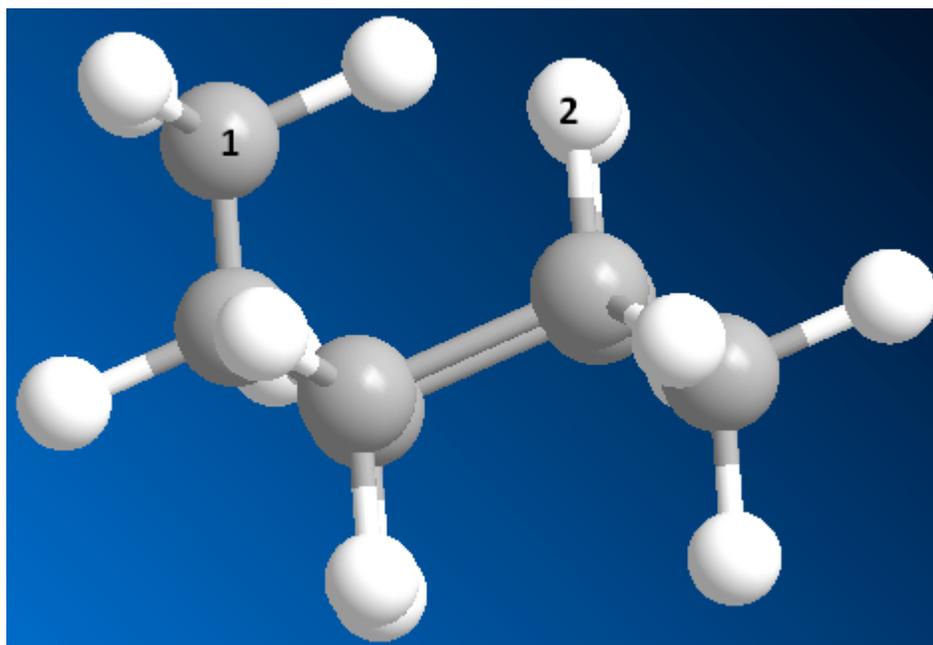
¹ Wikipedia, "Bent Bond". Wikipedia. April 22, 2008 <http://en.wikipedia.org/wiki/Bent_bond>.

² Hunt, Ian. "Conformational Analysis". University of Calgary. April 22, 2008 <<http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch03/ch3-ans.html>>.

This diagram shows cyclohexane in its chair conformation, with axial substituents marked “A” and equatorial substituents marked “E.”



The following diagram shows methylcyclohexane, demonstrating the 1, 3-diaxial interactions.

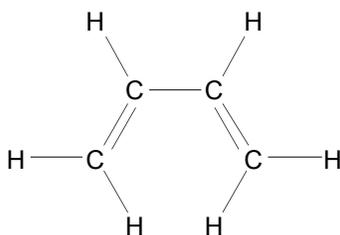


Notice the close approaches of the methyl group (1) and the two axially upward hydrogens (2) when the methyl group is axial. It is these steric repulsions that cause the axial conformation of methyl cyclohexane to be higher in energy than the equatorial conformation.

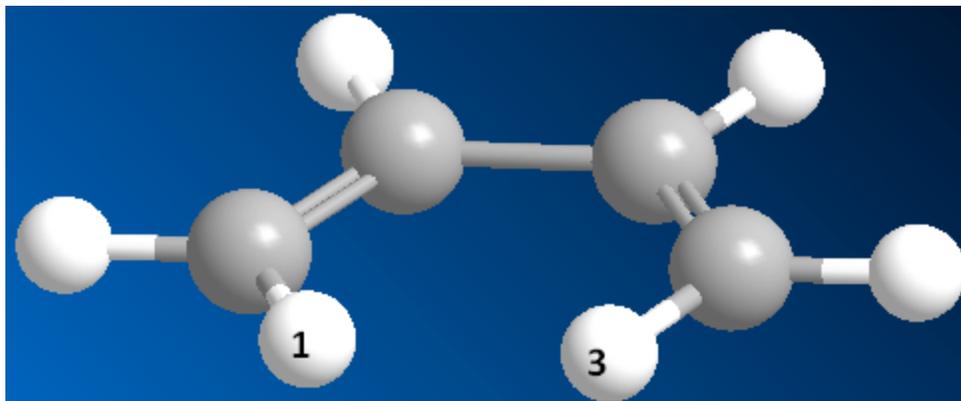
Let's see another example.

Example: 1, 3-butadiene

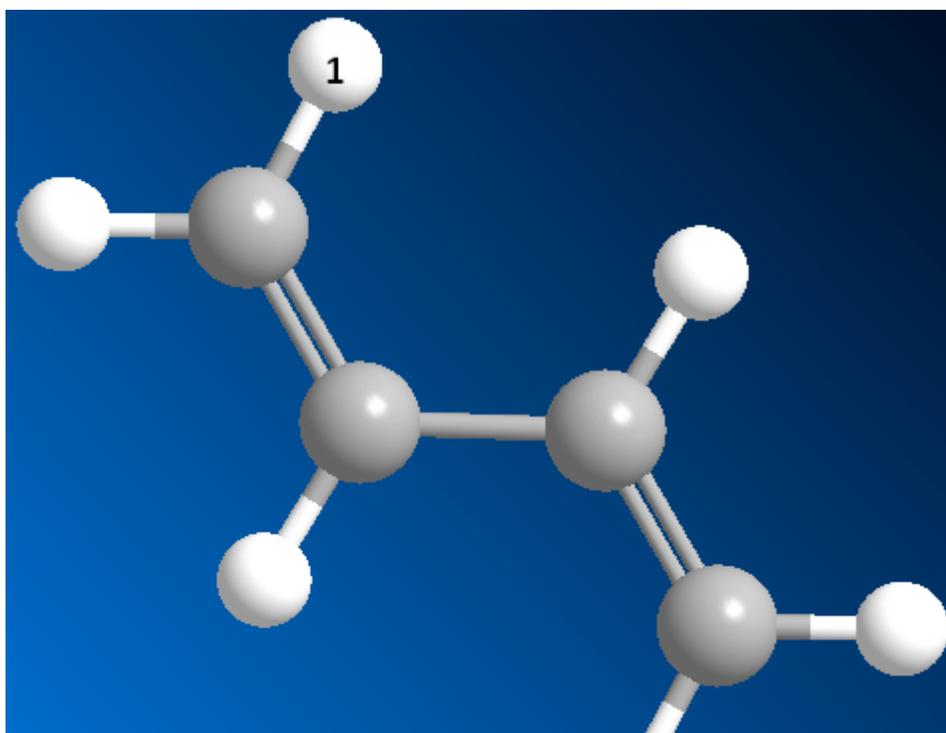
Here is the Lewis structure for 1, 3-butadiene:



This conformation of the molecule is referred to as the *s-cis* conformation. In this conformation, the hydrogens (labeled 1 and 3 in the diagram below) are in close proximity. Therefore, they have steric repulsions.



Because of steric repulsion, the preferred conformation of 1,3-butadiene is the *s-trans* form. The illustration below shows the *s-trans* conformation in which the repelling hydrogens (1 and 3) are far apart.

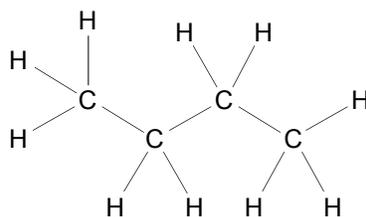


The third type of strain is called torsional strain, and is discussed below.

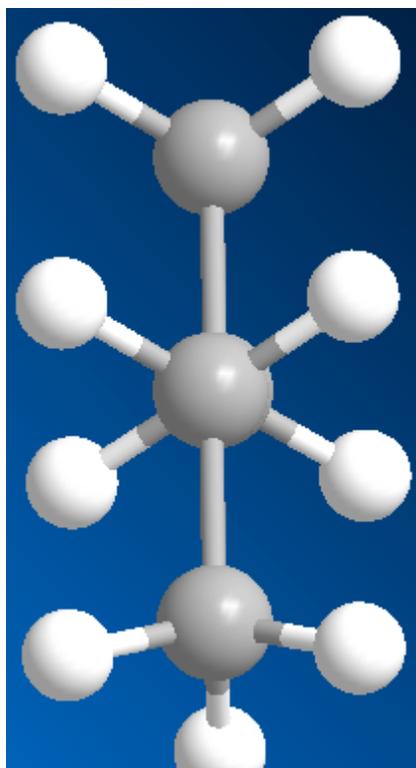
Torsional Strain: Torsional strain is steric strain that occurs when there are eclipsed or gauche interactions. Here's an example.

Example: butane

The Lewis structure for butane is shown below.



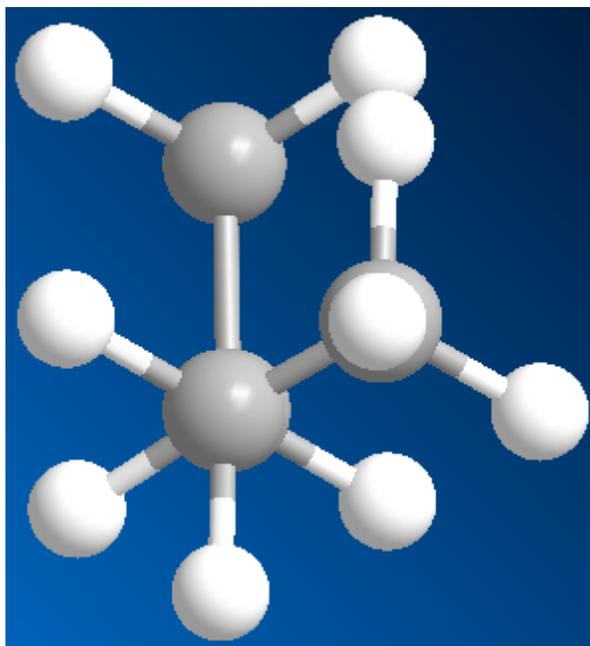
The following diagram shows a view of butane looking down the C2-C3 bond axis. Note that the configuration is anti.



Anti→

In this conformation, the torsional strain is minimized because the biggest groups are farthest apart from one another. Now let's analyze the torsional strain when the conformation is gauche, as is shown by the diagram below.

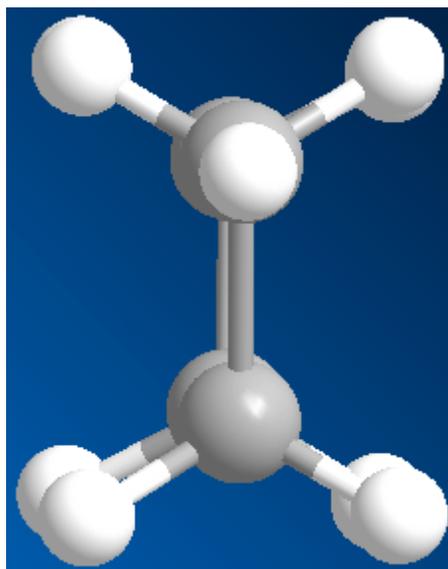
Gauche →



Notice that in the
the methyl groups are very close together.

gauche conformation,

The following diagram shows butane in the eclipsed conformation.



Eclipsed →

The eclipsed conformation has a very high energy because of the high amount of torsional strain because the methyl groups are in close proximity.

In summary, strain takes many different forms. It increases the potential energy stored within a molecule, thereby making the molecule less stable and more prone to higher reactivity.