

Strain

INTRODUCTION:

Compounds can come in all different arrangements and shapes. The arrangement of the different elements in the compound are influenced by the strain each element or compound experiences. A compound can experience three different types of strain: angular strain, torsional strain, and steric strain. Due to the interactions and repulsions between different molecules, a compound can consist of any, all, or none of these three strains.

VOCABULARY:

1. Strain: When a molecule is less stable due to electron repulsion or when it is not in its ideal geometry.
2. Torsional Strain: When rotating a molecule around a bond, the torsional strain is the repulsion caused by the electrons in between different groups when they pass by each other.
3. Steric Strain: Strain caused by the electrons in between different groups. Steric strain cannot be lessened by rotating the molecule around a bond.
4. Angle Strain: Strain caused when the actual bond angles in the atoms of the molecule differ from the ideal bond angles of their geometry.

There might be some confusion between torsional and steric strain; the difference is that "torsional strain can be relieved by bond rotation whereas steric strain cannot" (Thinkbook pg. 25)

TORSIONAL STRAIN:

When a molecule is able to rotate around a sigma bond, there is bound to be different levels of torsional strain that vary with the placements of the substituents relative to each other. This leads to different conformations of molecules (such as staggered or eclipsed) with different energy levels, which leads to different levels of stability. An example would be the molecule of butane. As we can see in the diagram below, the gauche and anti conformations are more stable than when the molecule is eclipsed.

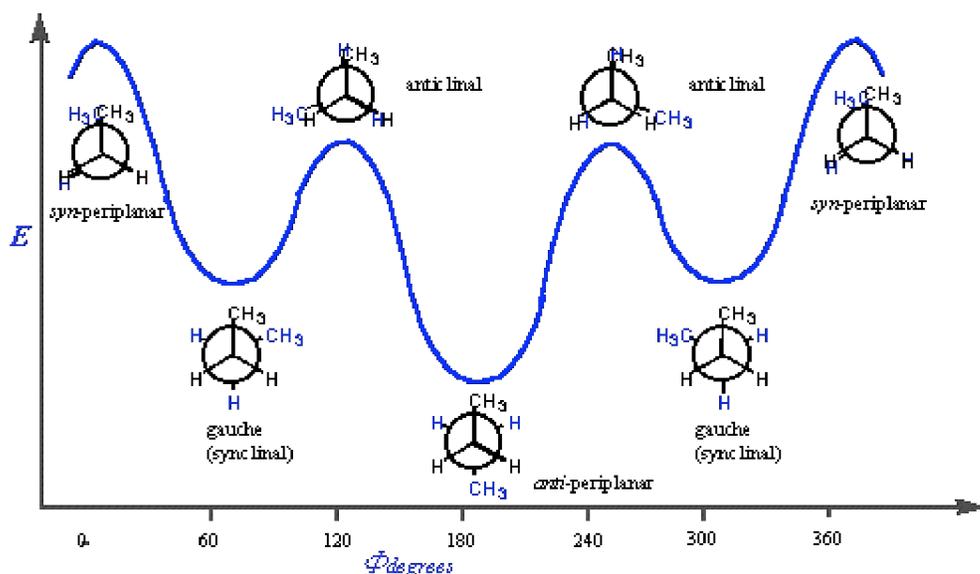


Image from <http://chemistry.anu.edu.au/Staff/RAB/Stereochem/Newman2.gif>

STERIC STRAIN:

Steric strain can also be referred to as steric hindrance, which is related to Van Der Waals repulsion, or the strain that occurs as the distance between two atoms or substituents decreases. Steric strain occurs when multiple substituents are close together, and cannot be separated by rotation.

To clarify the distinction between steric and torsional strain, it can be helpful to look at the arrangement of the substituents; if they are attached to neighboring carbons on acyclic molecules (an example would be the butane molecule shown in the diagram above) this is torsional strain. The torsional strain is more severe between two methyl groups (this is reflected in the higher-energy position of this conformation of butane) than the strain between an eclipsed methyl and hydrogen, which has a relatively lower energy.

To grasp the distinction between steric and torsional strain, draw the Newman projection of pentane (down the C2-C3 bond) and all of the possible conformations. In the gauche conformation, the interaction between the methyls 60 degrees apart from each other is steric because it cannot be relieved by rotation—other conformations will either be eclipsed or simply have the same

methyl interaction, only with variation in position. The eclipsed conformation, however, does have torsional strain—the methyl interaction can be immediately relieved after rotating to gauche, the most stable conformation. It is important to notice that gauche is *not free of strain*, but has relatively less strain than the other possible conformations.

Steric strain is most evident upon examining cyclic molecules; when substituents are bonded on neighboring (or possibly the same) carbon, the distance between them cannot be relieved without breaking a bond because the molecule is in a ring. A familiar example is the chair conformation of hexane—the most stable chair conformations have the largest substituents in the equatorial position. This is because in the axial position, these substituents are closer to other axial groups and steric strain will occur.

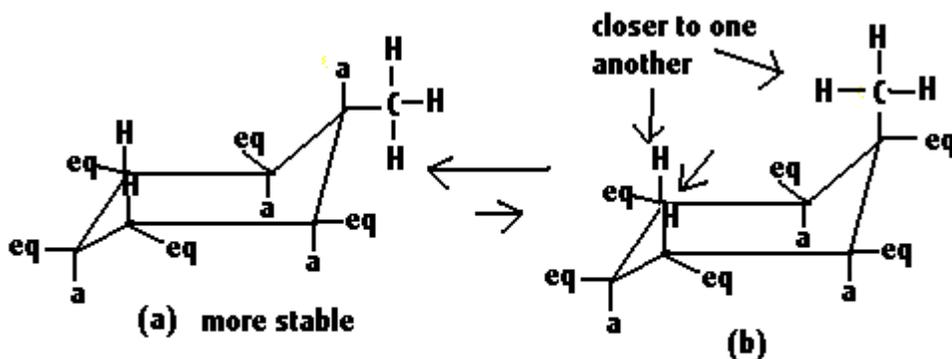


Fig 8- Methyl Cyclohexane Conformers

Image from <http://members.aol.com/logan20/conform.html>

ANGLE STRAIN:

Cyclic molecules are an excellent example to demonstrate angular strain. An element that has a very large amount of angle strain is cyclopropane as seen in the diagram below. As you can see, the carbons in cyclopropane want to be in 109.5° angles with each other. However, due to the geometry of the molecule, the carbons are forced into 60° angles with each other. This causes severe strain in the molecule.

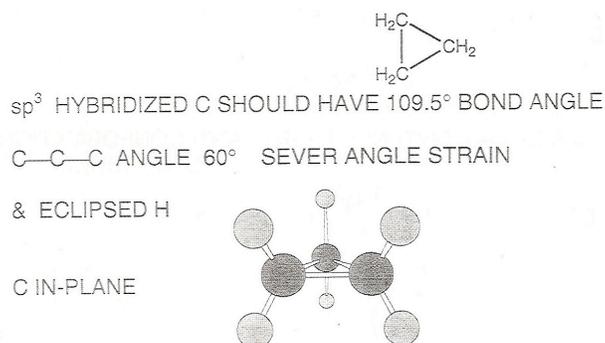


Image from Professor Lavelle's 14B course reader.

Cyclobutane is an example that contains angular and torsional strain. To relieve the angular strain, cyclobutane twists its structure into a conformation known as the butterfly conformation.

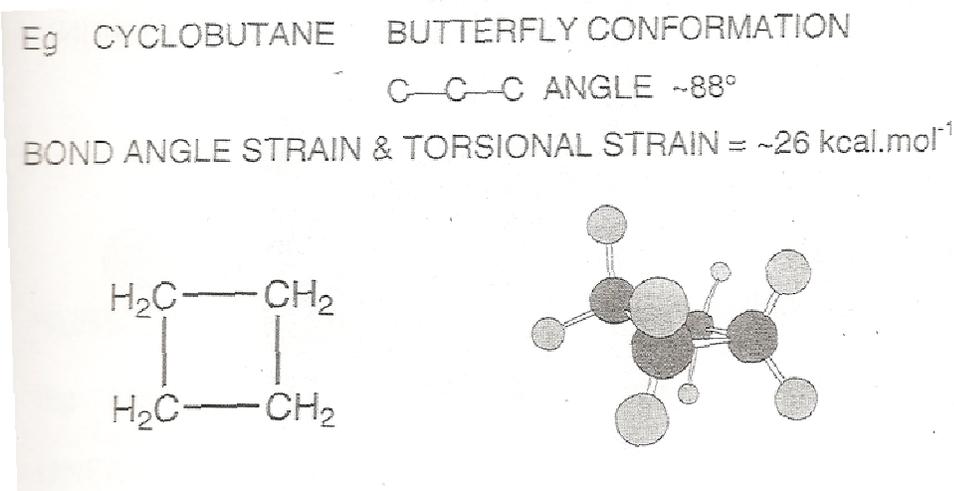


Image from Professor Lavelle's 14B course reader

IMPLICATIONS OF STRAIN

Conjugation:

It is important to note the role of strain when identifying conjugation in molecules. Because conjugation requires planarity to allow for parallel, overlapping, adjacent p-orbitals, it is possible that a molecule will have a very high level of torsional strain when in a planar conformation. This strain will outweigh the potential increased stability.

Note: The energy a molecule in kcal/mol is experimentally determined; we can infer that the decrease in energy that results from conjugation would be lower than the increase in energy due to steric or torsional strain. Though we cannot know the precise numbers, the questions in the Thinkbook that deal with this exception make it very clear that there is a significant amount of torsional strain because the nearby substituents are very large.

An example would be comparing the *s-cis* and *s-trans* conformations of the following molecule:

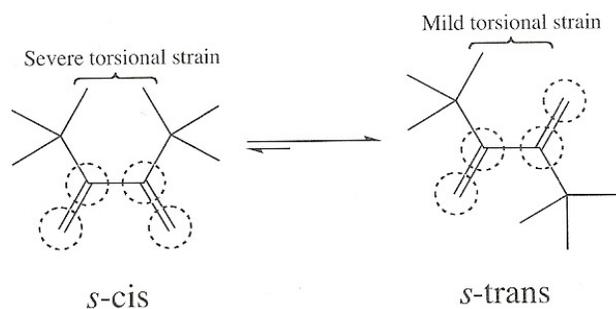


Image from Dr. Hardinger's 14C Thinkbook pg. 60

The *s-cis* molecule will not be conjugated because maintaining a planar conformation causes more torsional strain than any reduction in energy due to conjugation.