Conformational Isomers

Different structures of a molecule that result from rotation about sigma bonds are known as conformational isomers, or conformers. Two conformational isomers of ethane appear here.

Conformational Isomers and Configurational Isomers

Conformational isomers (conformers) interconvert through rotation about sigma bonds, a low-energy process.

Configurational isomers interconvert through the breaking and reforming of covalent bonds, a high-energy process.

The Newman Projection

The sawhorse projection, a perspective view of a conformation.

The Newman projection, and end-on view of a conformation.

Staggered and Eclipsed Conformations of Ethane

Staggered - Hydrogens are farthest from each other; the lowest energy conformation.

Eclipsed - Hydrogens are closest to each other; the highest energy conformation.

The two conformations differ in energy by 3 x 4.0 kJ/mol = 12.0 kJ/mol.
Conformations of Propane

The shape of the energy vs. rotation curve for propane is the same as for ethane, but the trough-to-peak energy difference is greater for propane, due to eclipsed methyl-hydrogen interaction.

Conformations of Butane

With the CH₃ groups as far apart as possible, the anti conformation has the lowest energy.

Gauche is intermediate in energy.

CH₃/CH₃ eclipsing produces the highest-energy conformation.
Conformational Analysis of Butane

Energies of Two Eclipsed Butanes

Energy Costs for Interactions in Alkane Conformations

The Bayer Strain Theory - Background

The Bayer Strain Theory (1885) - Summary
Baeyer Strain Theory - Predictions

What's the internal angle of cyclohexane? By what value does this differ from the tetrahedral angle? What's the internal angle of an infinitely large cycloalkane?

The Baeyer Strain Theory - Experimental Observations

The Baeyer Strain Theory Today

Baeyer's theory was wrong for a very simple reason. He assumed that rings are flat. In fact, though, most cycloalkanes are not flat; they adopt puckered, three-dimensional conformations that allow bond angles to be nearly tetrahedral. Only for three- and four-membered rings is the concept of angle strain important.

One of Two Chair Conformations of Cyclohexane

Axial and Equatorial Hydrogens in Chair Cyclohexane

Chair Cyclohexane - A View From The Top
Chair Cyclohexane - A Newman Projection

Red hydrogens are axial
Blue hydrogens are equatorial
Two equatorial hydrogens are not shown in the Newman projection of cyclohexane.

Interconversion of The Two Chair Conformers of Cyclohexane

The axial substituents of one chair conformation become equatorial in the other chair conformation.
The equatorial substituents of one chair conformation become axial in the other chair conformation.

Newman Projections of the Chair-Chair Interconversion

Axial and equatorial substituents interchange as one chair conformation flips to the other chair conformation.

Alkylcyclohexanes

Ring-flip allows the alkyl group to occupy either an axial or an equatorial position.
Steric interference occurs between an axial alkyl group and axial hydrogens.
Molecular energy is lowest with the alkyl group in the equatorial position.

Both Chair Conformers of Methylcyclohexane

The conformer bearing the equatorial -CH₃ is lower in energy than the conformer bearing the axial -CH₃ group.
The equilibrium favors the isomer with the equatorial -CH₃ group.
Conformers of **cis-1,2-Dimethylcyclohexane**

*Con* - In each conformer one CH$_3$ is axial, one is equatorial.

Conformers of **trans-1,2-Dimethylcyclohexane**

*Trans* - Both CH$_3$ groups are axial in one conformer, equatorial in the other.

Conformers of **trans-1,2-Dimethylcyclohexane**

Since both CH$_3$ groups can be equatorial in the *trans* geometric isomer, the *trans* is the lower-energy geometric isomer.

**cis- and trans-1,2-Dimethylcyclohexane**

Because both CH$_3$ groups can occupy equatorial positions in the *trans* configuration, the *trans* configuration contains less strain energy than the *cis*.

**cis- and trans-1,3-Dimethylcyclohexane**

*Here, because both CH$_3$ groups can occupy equatorial positions in the *cis* configuration, the *cis* configuration contains less strain energy than the *trans*.*

**cis- and trans-1,4-Dimethylcyclohexane**

For 1,2-dimethylcyclohexane, the *trans* geometric isomer has the lesser amount of strain energy.

For 1,3-dimethylcyclohexane, the *cis* geometric isomer has the lesser amount of strain energy.

For 1,4-dimethylcyclohexane ?????
Boat Cyclohexane
A high-energy conformation of cyclohexane
Will not consider in detail

Polycyclic Molecules - Decalin
A polycyclic molecule contains two or more rings.
Fused rings share one or more sides.
Bridgehead atoms are incorporated into two or more rings.

Decalin (two fused cyclohexane rings)

 cis- and trans-Decalin
 trans-Decalin - Bridgehead H's are trans to each other;
lower energy isomer.
 cis-Decalin - Bridgehead H's are cis to each other;
higher energy isomer.
Less crowding of H's in the trans isomer

More Complex Fused-Ring Compounds - Testosterone; A Steroid; A Sex Hormone
Testosterone (a steroid)

End
Stereochemistry of Alkanes and Cycloalkanes