

Conformations of Alkanes and Cycloalkanes

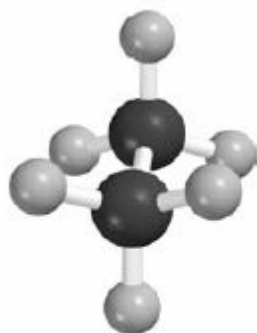
SUMMARY

In this chapter we explored the three-dimensional shapes of alkanes and cycloalkanes. The most important point to be taken from the chapter is that a molecule adopts the shape that minimizes its total **strain**. The sources of strain in alkanes and cycloalkanes are:

1. **Bond length distortion:** destabilization of a molecule that results when one or more of its bond distances are different from the normal values
2. **Angle strain:** destabilization that results from distortion of bond angles from their normal values
3. **Torsional strain:** destabilization that results when adjacent atoms are not staggered
4. **Van der Waals strain:** destabilization that results when atoms or groups on nonadjacent atoms are too close to one another

The various spatial arrangements available to a molecule by rotation about single bonds are called **conformations**, and **conformational analysis** is the study of the differences in stability and properties of the individual conformations. Rotation around carbon-carbon single bonds is normally very fast, occurring hundreds of thousands of times per second at room temperature. Molecules are rarely frozen into a single conformation but engage in rapid equilibration among the conformations that are energetically accessible.

Section 3.1 The most stable conformation of ethane is the **staggered** conformation. It is approximately 12 kJ/mol (3 kcal/mol) more stable than the **eclipsed**, which is the least stable conformation.



Staggered conformation of ethane
(most stable conformation)

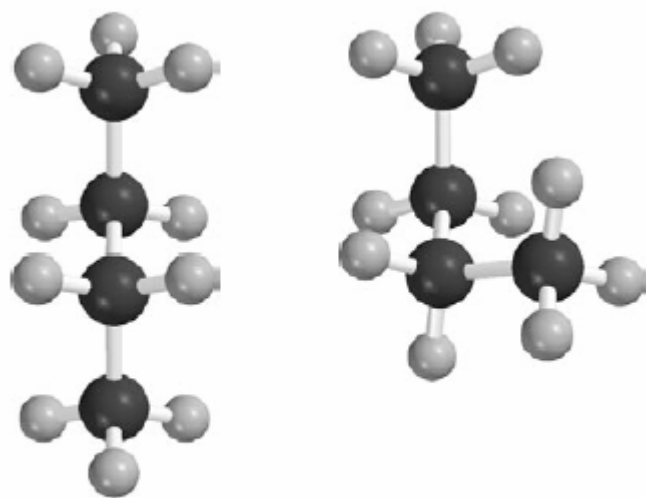


Eclipsed conformation of ethane
(least stable conformation)

The difference in energy between the staggered and eclipsed forms is due almost entirely to the torsional strain in the eclipsed conformation. At any instant, almost all the molecules of ethane reside in the staggered conformation.

Section 3.2

The two staggered conformations of butane are not equivalent. The **anti** conformation is more stable than the **gauche**.

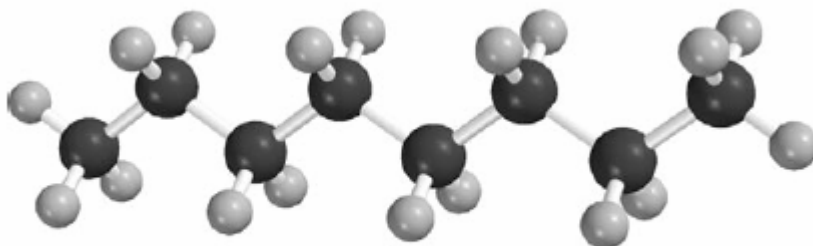


Anti conformation of butane Gauche conformation of butane

Neither conformation suffers torsional strain, because each has a staggered arrangement of bonds. The gauche conformation is less stable because of van der Waals strain involving the methyl groups.

Section 3.3

Higher alkanes adopt a zigzag conformation of the carbon chain in which all the bonds are staggered.



Octane

Section 3.4

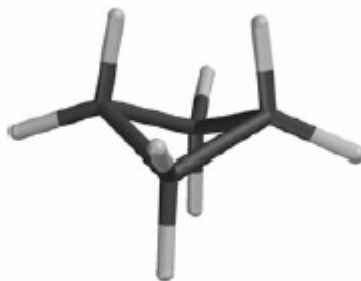
At one time all cycloalkanes were believed to be planar. It was expected that cyclopentane would be the least strained cycloalkane because the angles of a regular pentagon (108°) are closest to the tetrahedral angle of 109.5°. Heats of combustion established that this is not so. With the exception of cyclopropane, the rings of all cycloalkanes are nonplanar.

Section 3.5

Cyclopropane is planar and destabilized by angle strain and torsional strain. Cyclobutane is nonplanar and less strained than cyclopropane.



Cyclopropane



Cyclobutane

Section 3.6 Cyclopentane has two nonplanar conformations that are of similar stability: the **envelope** and the **half-chair**.



Envelope conformation of cyclopentane



Half-chair conformation of cyclopentane

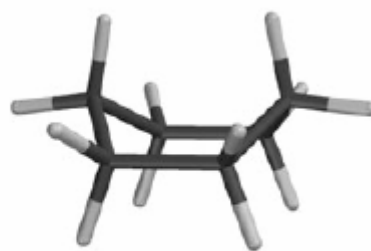
Section 3.7 Three conformations of cyclohexane have approximately tetrahedral angles at carbon: the chair, the boat, and the skew boat. The chair is by far the most stable; it is free of torsional strain, but the boat and skew boat are not. When a cyclohexane ring is present in a compound, it almost always adopts a chair conformation.



Chair



Skew boat



Boat

Section 3.8 The COH bonds in the chair conformation of cyclohexane are not all equivalent but are divided into two sets of six each, called **axial** and **equatorial**.

Section 3.10

3.9

A

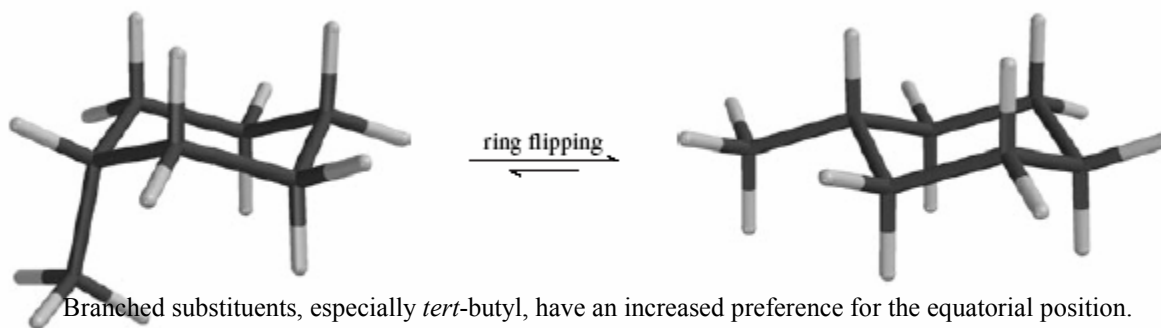


Axial bonds to H in cyclohexane



Equatorial bonds to H in cyclohexane

substituent is less crowded and more stable when it is equatorial than when it is axial on a cyclohexane ring. Ring flipping of a monosubstituted cyclohexane allows the substituent to become equatorial.



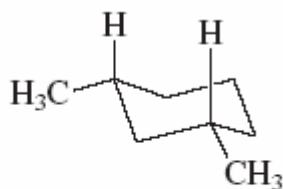
Branched substituents, especially *tert*-butyl, have an increased preference for the equatorial position.

Methyl group axial (less stable)

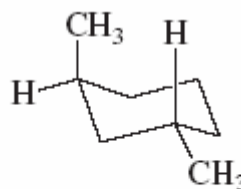
Methyl group equatorial (more stable)

Sections 3.11–3.12

Stereoisomers are isomers that have the same constitution but differ in the arrangement of atoms in space. *Cis*- and *trans*-1,3-dimethylcyclohexane are stereoisomers. The *cis* isomer is more stable than the *trans*.



Most stable conformation of *cis*-1,3-dimethylcyclohexane (no axial methyl groups)



Most stable conformation of *trans*-1,3-dimethylcyclohexane (one axial methyl group)

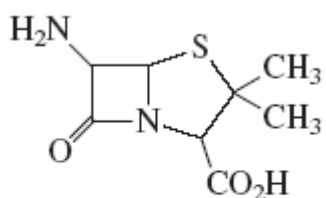
Section 3.13

Higher cycloalkanes have angles at carbon that are close to tetrahedral and are sufficiently flexible to adopt conformations that reduce their torsional strain. They tend to be populated by several different conformations of similar stability.

Section 3.14

Cyclic hydrocarbons can contain more than one ring. **Spiro** hydrocarbons are characterized by the presence of a single carbon that is common to two rings. **Bicyclic** alkanes contain two rings that share two or more atoms.

Section 3.15 Substances that contain one or more atoms other than carbon as part of a ring are called **heterocyclic** compounds. Rings in which the heteroatom is oxygen, nitrogen, or sulfur rank as both the most common and the most important.



6-Aminopenicillanic acid
(bicyclic and heterocyclic)