

# Alkanes

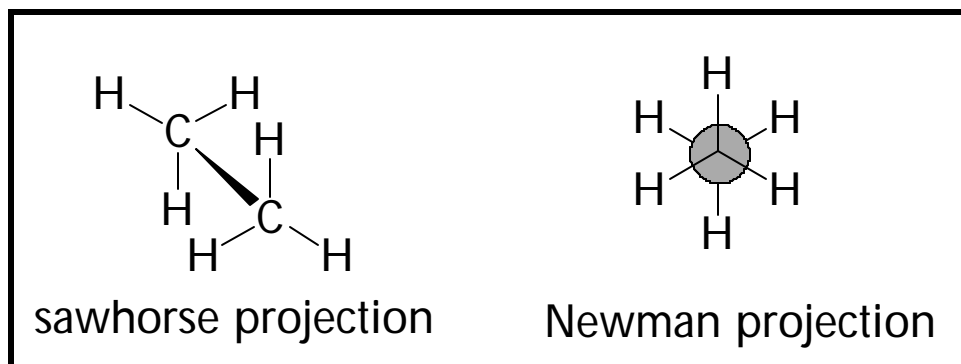
Carbons are  $sp^3$  hybridized.

Bonds are  $\sigma$ -bonds. C-C bonds  $\sim 1.54\text{\AA}$ ;

C-H bonds  $\sim 1.10\text{\AA}$ .

Bond angles  $\sim 109^\circ$ .

Ethane —



Different arrangements of atoms in a molecule convertible into one another by rotation of groups of atoms about single bonds are called *conformations*. If the energy barrier to the rotation is nil or small, the rotation is said to be free or almost free.

The rotation of the methyl groups around the C-C bond in ethane is almost free; therefore, ethane can exist in an infinite number of conformations.

As one methyl group rotates relative to the other the energy of the molecule does change; the *staggered conformation* has the lowest energy and the *eclipsed conformation* has the highest energy.

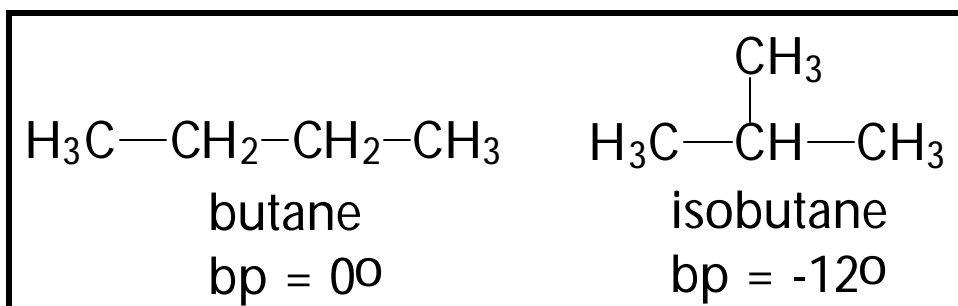
Eclipsed conformation has *torsional strain* — probably due to repulsions between electrons in the C-H bonds on C-1 and on C-2.

Propane —  $C_3H_8$

Rotational barrier ~ 14kJ/mole (3.3 kcal/mole): torsional strain.

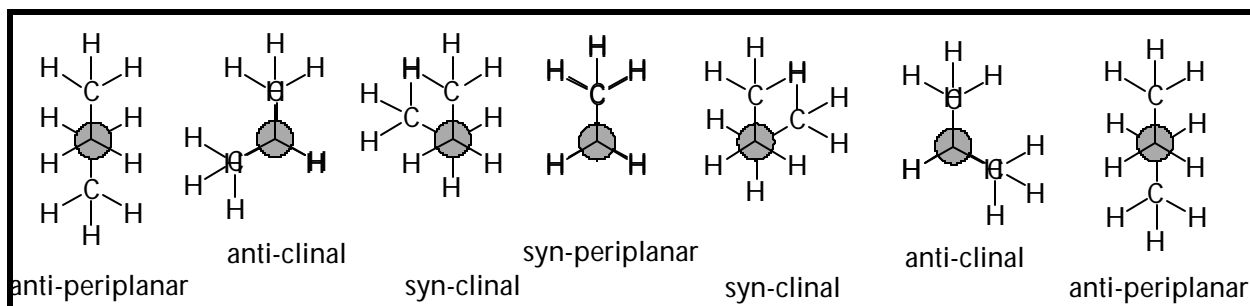
Butane —  $C_4H_{10}$

Two structural isomers —



Let's examine *butane* by sighting down the C-2 to C-3 bond of the staggered conformation in which the methyl groups are  $180^\circ$  apart. Then we will rotate the rear ethyl group clockwise around the C-2 to C-3 bond until the methyl groups are again  $180^\circ$  apart. There will be an infinite number of conformations, but we will focus our attention on the staggered and eclipsed ones.

Sometimes the different conformations are named as follows:



Strain —

anti-periplanar: none

anti-clinal: torsional ~ propane

synclinal: steric

☞ methyl groups begin to approach each other,  
less strain than anti-clinal.

syn-periplanar: steric and torsional

most strained conformation



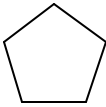
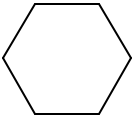
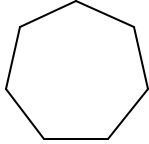
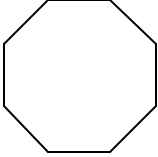
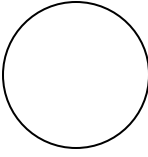
## Cycloalkanes

Adolf von Baeyer, cycloalkanes, and *angle strain* —

The interior angles of regular polygons are given by the following formula:

$$\text{angle} = 180(n - 2)/n,$$

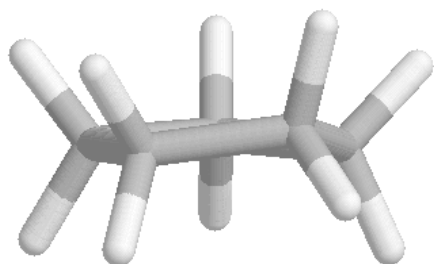
where  $n$  is the number of sides to the polygon

Sizes of Interior Angles in Degrees						
						
60	90	108	120	129	135	180

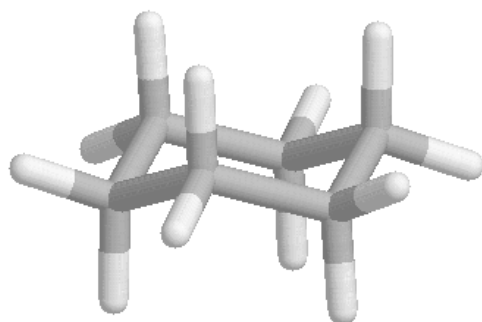
The natural angle for tetrahedral carbon is  $109^\circ$ . Rings of 5 and 6 carbon atoms occur commonly in nature; rings of other sizes are less common. Baeyer reasoned that five and six-membered rings were common because they did not have much angle strain and therefore were more stable (contained less energy) than the other rings, which deviated from  $109^\circ$  by greater amounts.

Bayer was right about the 3- and 4-member rings having angle strain. (They also have torsional strain because the C-H bonds are eclipsed or partially eclipsed.) However, rings larger than this are not planar; they pucker (even the 4-member ring does this to some extent). By doing this, rings of 5 or more carbons actually have bond angles very close to  $109^\circ$  and no angle strain. Examples follow.

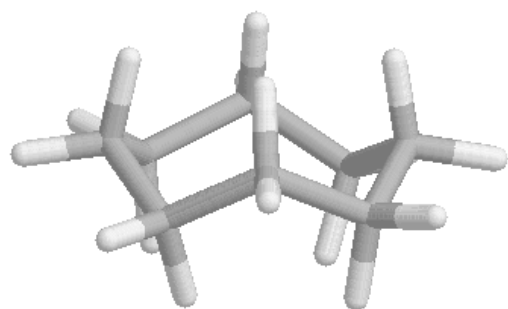
Five member ring –

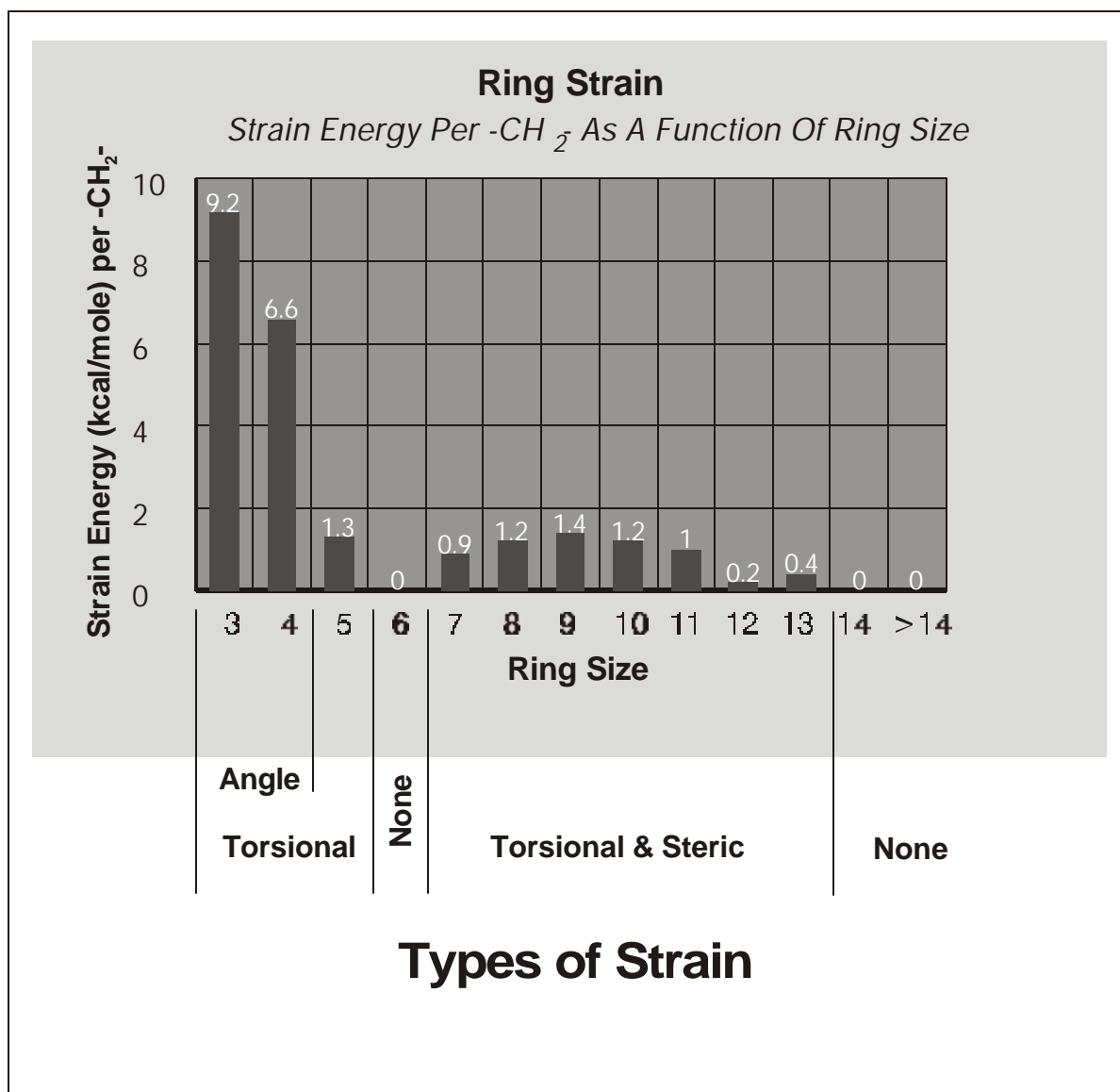


Six member ring –



Eight member ring –





The strain that does exist in rings of size 7-13 is a combination of torsional and steric strain. All of this is best seen using molecular models.

## Configurational Stereoisomers

Different conformations of a molecule are, in a sense, isomers: they have the same molecular formula, but are not identical. They differ in regard to the orientation of atoms in space, not atomic connections: **stereoisomers**.

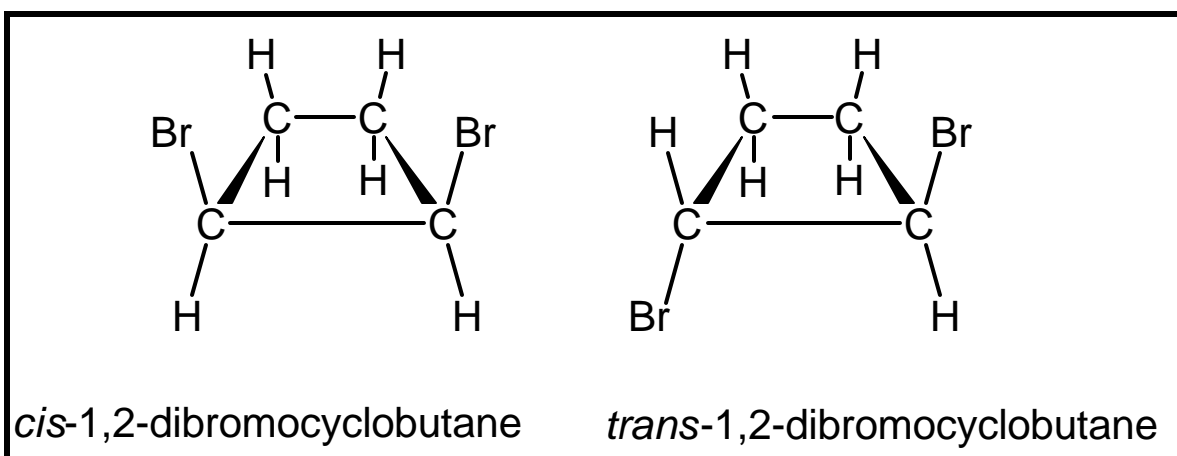
Stereoisomers that interconvert by rotation around single bonds are conformational stereoisomers.

### Cyclic Compounds —



Because of the ring, there is not 360° free rotation around single bonds which are part of the ring.

This leads to stereoisomers that do not interconvert — configurational stereoisomers.

(The term stereoisomer, without modifier, means configurational.)



## Cyclohexane — Chair Conformation

- < No angle strain ( $\sim 109^\circ$ ).  
No torsional strain: totally staggered.  
See McMurry, 4<sup>th</sup> ed., Fig. 2.14, pg. 63, or (better) make a model.
- < Two types of bonds: *axial* and *equitorial*.  
Axial: parallel to axis of circumscribed sphere;  
three up, three down --- alternating.  
Equitorial: projecting from equator of sphere.  
See McMurry, 4<sup>th</sup> ed., Fig. 2.15, pg. 64, or (better) make a model.
- < Draw it:
  - 1) parallel lines: / /,
  - 2)  on top,
  - 3)  on bottom,
  - 4) equitorial bonds parallel to ring bonds,
  - 5) axial bonds up and down to make tetrahedral carbons.
- < *Ring-flip*: a conformational change. Axial groups become equitorial; equitorial become axial.  
See McMurry, 4<sup>th</sup> ed., Fig. 2.16, pg 65 or (much better) make a model.



- < Substituted cyclohexanes: substituent groups are more stable in equatorial positions owing to *1,3-diaxial interactions* (steric strain) when they are axial. The larger the group the greater the 1,3-diaxial interactions.

In most cases, if a cyclohexane has a *t*-butyl substituent almost all molecules will have the *t*-butyl equatorial.

See McMurry, 4<sup>th</sup> ed., Fig. 2.17, pg. 66.