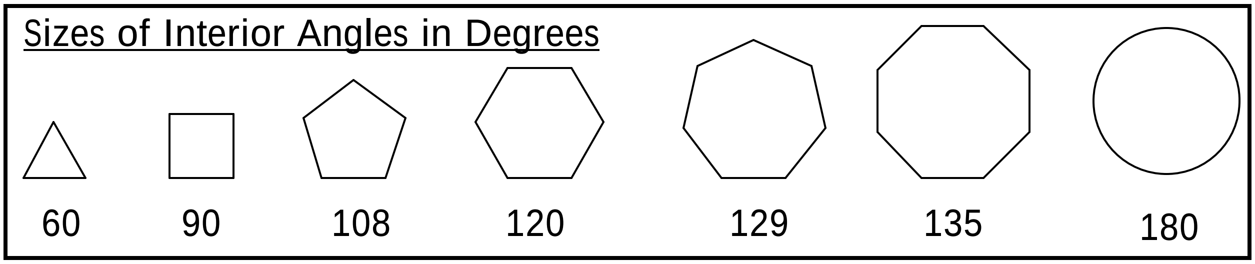
Cycloalkanes

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

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

angle = 180(n -2)/n,
where n is the number of sides to the polygon



The natural angle for tetrahedral carbon is 109^o. 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^o by greater amounts.

But great theories are sometimes brought down by experimentation.

Let's consider several acyclic alkanes — no rings, therefore, no strain energy.

Burn each of them to form carbon dioxide and water and measure the heat of combustion.

Compound	ΔH, kcal/mole	$\Delta\Delta$H, kcal/mole
propane-C_3H_8	530.4	
		157.4
butane-C_4H_{10}	687.8	
		157.2
pentane-C_5H_{12}	845.0	
		157.6
hexane-C_6H_{14}	1002.6	
Average		157.4

So, the average heat of combustion for a CH_2 unit in an unstrained alkane is 157.4 kcal/mole. We might write:

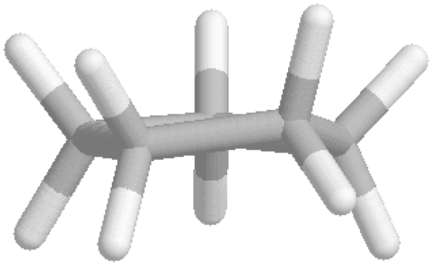
$$n\ CH_2 + n(3/2)\ O_2 \text{ ------->} \qquad n\ CO_2 + n\ H_2O + n(157.4\text{ kcal})$$

Strained rings, which have more energy than unstrained ones, should give off more heat per CH_2 unit when they are burned to give carbon dioxide and water. Let's see.

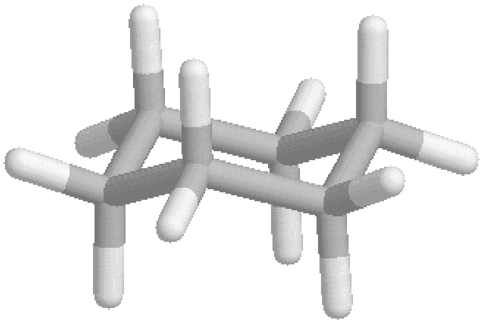
$(CH_2)_n$	ΔH, kcal/mol	$\Delta H/CH_2$, kcal/mol	Strain energy/CH_2
$(CH_2)_3$	499.8	166.6	9.2
$(CH_2)_4$	655.9	164.0	6.6
$(CH_2)_5$	793.5	158.7	1.3
$(CH_2)_6$	944.5	157.4	0
$(CH_2)_7$	1108	158.3	0.9
$(CH_2)_8$	1269	158.6	1.2
$(CH_2)_9$	1429	158.8	1.4
$(CH_2)_{10}$	1586	158.6	1.2
$(CH_2)_{11}$	1742	158.4	1.0
$(CH_2)_{12}$	1891	157.6	0.2
$(CH_2)_{13}$	2051	157.8	0.4
$(CH_2)_{14}$	2204	157.4	0

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^o and no angle strain. 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. Three examples follow.

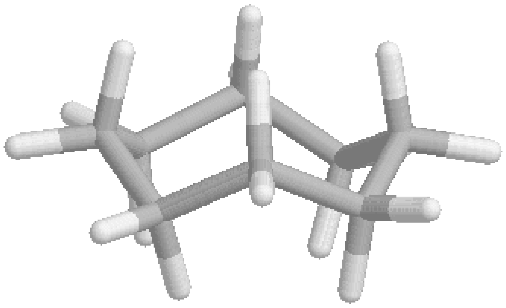
Five member ring – torsional strain only.

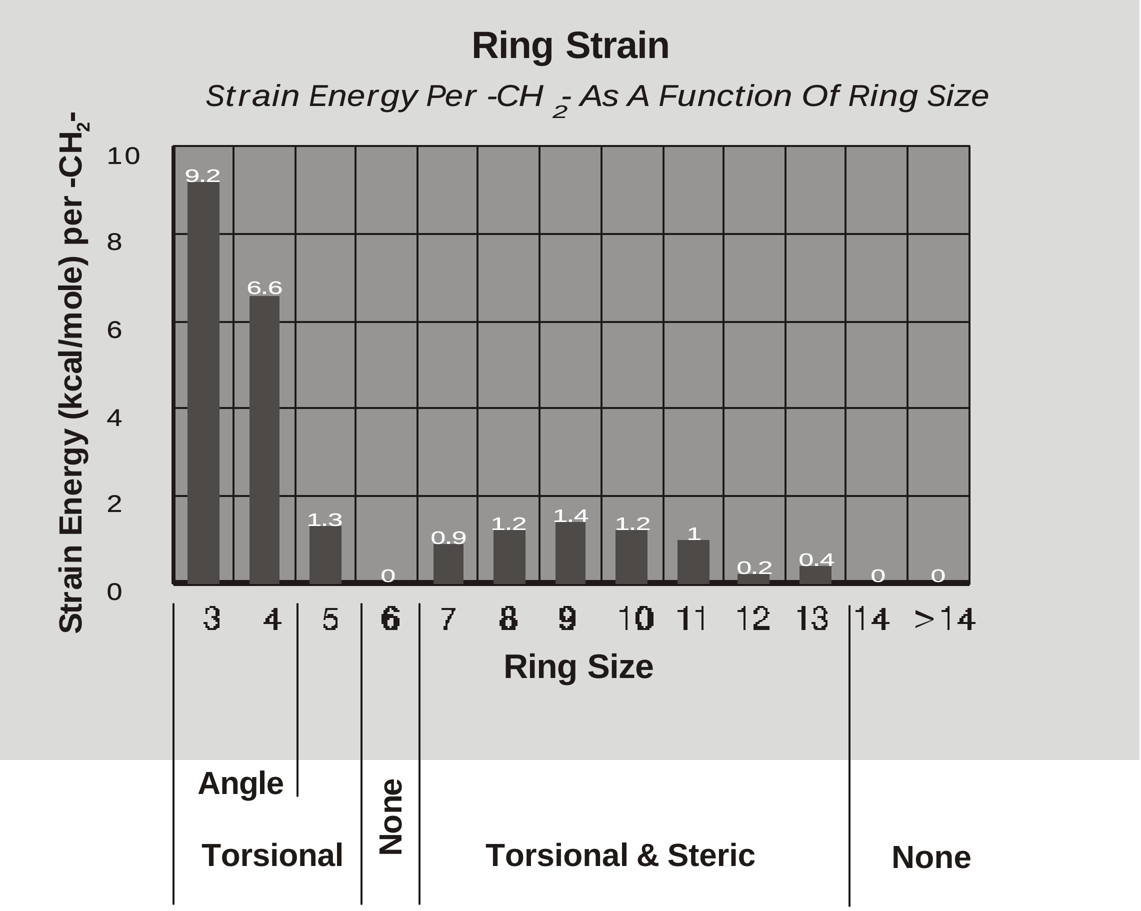


Six member ring – no strain in chair conformation shown.



Eight member ring – torsional and steric strain.





Types of Strain

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**.

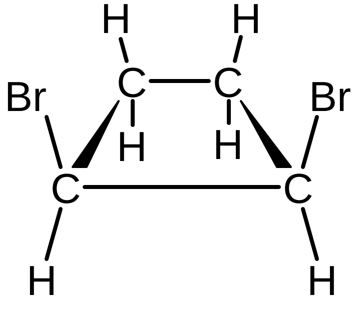
Stereoisomers that interconvert by rotation around single bonds are *conformational stereoisomers.*

Cyclic Compounds —

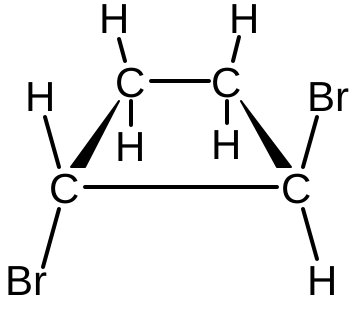
Because of the ring, there is not 360° free rotation around single bonds which are part of the ring.

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

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

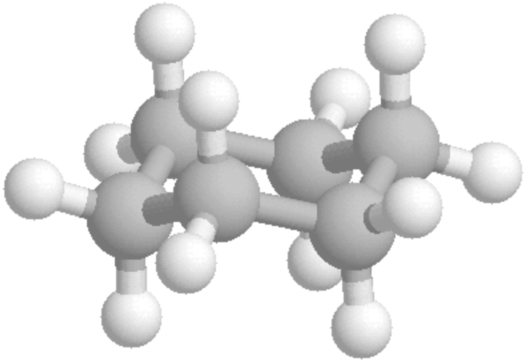


cis-1,2-dibromocyclobutane



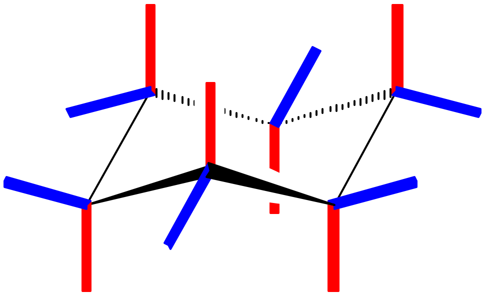
trans-1,2-dibromocyclobutane

Cyclohexane — Chair Conformation



>> No angle strain (~109°).
No torsional strain: totally staggered.
See McMurry, 5th ed., Fig. 4.13, pg. 128, 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, 5th ed., Fig. 4.15 - 4.17, pg. 130-31, or (better) make a model.



\>> Draw it —

1) parallel lines: /   /,
2)  on top,
3)  on bottom,
4) equitorial bonds parallel to ring bonds, one removed,
5) axial bonds up and down to make tetrahedral carbons.

\>> *Ring-flip*: a conformational change. Axial groups become equitorial; equitorial become axial.
See McMurry, 5th ed., Fig. 4.18, pg 132 or (much better) make a model.

\>> Substituted cyclohexanes: substituent groups are more stable in equitorial 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 equitorial.

See McMurry, 5th ed., Fig. 4.20, pg. 135.

\>> Analysis of disubstituted cyclohexanes —
cis-1,2 — axial/equitorial >flip> equitorial/axial
trans-1,2 — diequitorial >flip> diaxial

cis-1,3 — diaxial >flip> diequitorial
trans-1,3 — axial/equitorial >flip> equitorial/axial

cis-1,4 — axial/equitorial >flip> equitorial/axial
trans-1,4 — diequitorial >flip> diaxial

Make models; flip ring!

Cyclohexane — Boat Conformation

\>> No angle strain (~109°).
Torsional strain: eclipsed hydrogens.
Steric strain: bowsprint – flagpole hydrogens.
Some torsional/steric strain removed by twist-boat.

See McMurry, 5th ed., Fig. 4.23 & 4.24, pg. 140-41, or make a model.