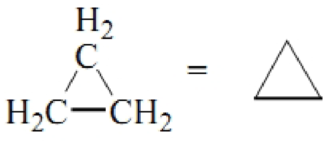
1. Alicyclic Hydrocarbons:

In the compounds that the carbon atoms are attached to one another to form chains; these are called open-chain compounds (**acyclic compounds**), and when the carbon atoms are arranged to form rings; these are called alicyclic compounds (**aliphatic cyclic hydrocarbons**) is an organic compound that is both aliphatic and cyclic. They contain one or more all-carbon rings which may be either saturated or unsaturated, but do not have aromatic character. Alicyclic compounds may have one or more aliphatic side chains attached.

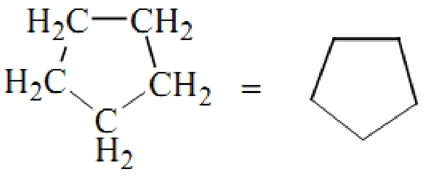
1.1 Nomenclature:

Cyclic aliphatic hydrocarbons are named by prefixing cyclo- to the name of the corresponding open-chain hydrocarbon having the same number of carbon atoms as the ring. For example:

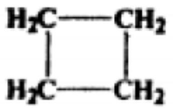
1. Cycloalkanes with only one ring:



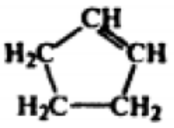
Cyclopropane



Cyclopentane

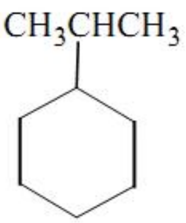


Cyclobutane



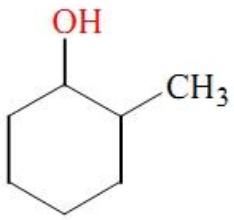
Cyclopentene

1) Substituted cycloalkanes: ***alkylcycloalkanes, halocycloalkanes, alkylcycloalkanols***
2) Number the ring ***beginning with the substituent first in the alphabet***, and number in the direction that gives the next substituent the **lower number** possible.
3) When **three or more** substituents are present, begin at the substituent that **leads to the lowest set of locants.**

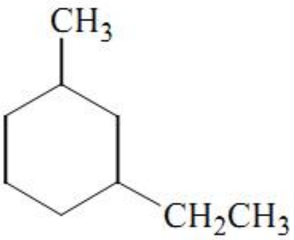


Isopropylcyclohexane

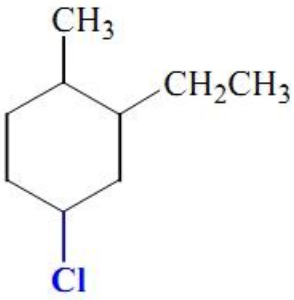
Chlorocyclopentane



2-Methylcyclohexanol

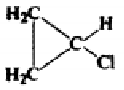


1-Ethyl-3-methylcyclohexane
(not **1-ethyl-5-methylcyclohexane**)



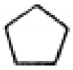
4-Chloro-2-ethyl-1-methylcyclohexane
(not **1-Chloro-3-ethyl-4-methylcyclohexane**)

Substituents on the ring are named, and their positions are indicated by numbers, the lowest combination of numbers being used, in simple cycloalkenes and cycloalkynes the doubly- and triply-bonded carbons are considered to occupy positions 1 and 2. For example:



Chlorocyclopropane

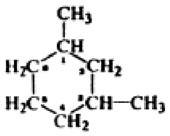
3-Ethylcyclopentene



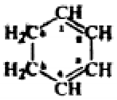
Cyclopentane

3-Ethylcyclopentene

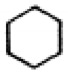
1,3-Cyclopentadiene



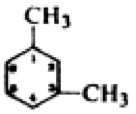
1,3-Dimethylcyclohexane



1,3-Cyclohexadiene



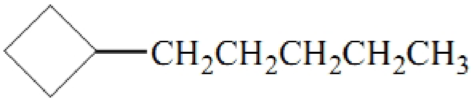
Cyclohexane



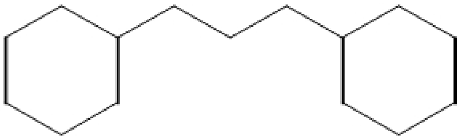
1,3-Dimethylcyclohexane

1,3-Cyclohexadiene

2. When a single ring system is attached to a single chain with a greater number of carbon atoms, or when more than one ring system is attached to a single chain:

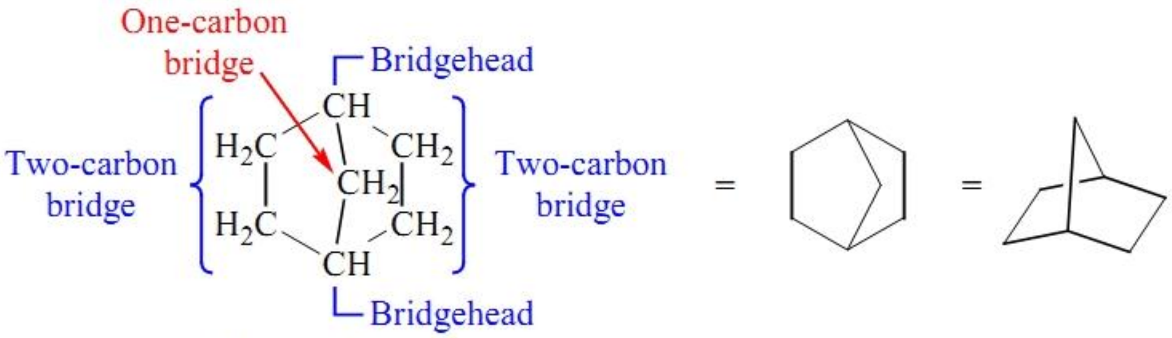


1-Cyclobutylpentane



1,3-Dicyclohexylpropane

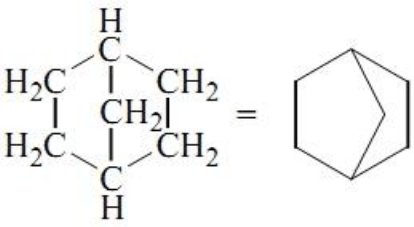
Polycyclic compounds **(bridgehead compounds)** contain two or more rings that share two or more carbon atoms. We can illustrate the naming system with norbornane, whose systematic name is bicyclo[2.2.1]heptane:



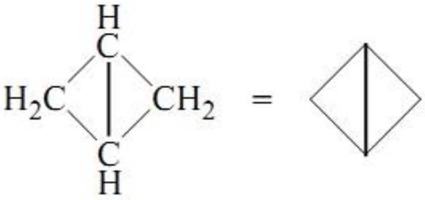
A bicycloheptane

(a) heptane, since it contains a total of seven carbon atoms; (b) bicyclo, since it contains two rings, that is, breaking two carbon-carbon bonds converts it into an open-chain compound; (c) [2.2.1], since the number of carbons between bridgeheads (shared carbons) is two (C-2 and C-3), two (C-5 and C-6), and one (C-7):

1) The **number of carbon atoms** in **each bridge** is interposed in brackets **in order of decreasing length**.

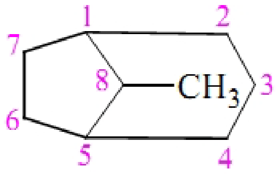


Bicyclo[2.2.1]heptane
(also called **norbornane**)

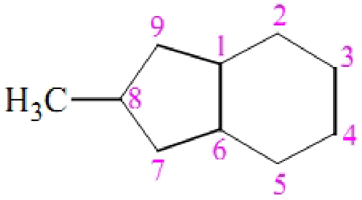


Bicyclo[1.1.0]butane

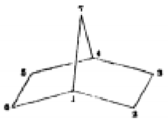
2) Number the bridged ring system **beginning at one bridgehead**, proceeding **first along the longest bridge** to **the other bridgehead**, then **along the next longest bridge** to **the first bridgehead**.



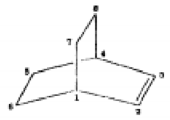
8-Methylbicyclo[3.2.1]octane



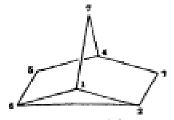
8-Methy;bicyclo[4.3.0]nonane



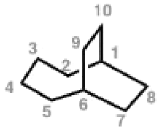
Bicyclo[2.2.1]heptane



Bicyclo[2.2.2]octa-2-ene



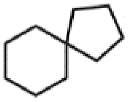
Tricyclo[2.2.1.$0^{2,6}$]heptane



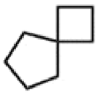
10 carbon alkane: **decane**
Bridge lengths: 4, 2, 2

bicyclo[4.2.2]decane

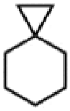
In **spirocyclic compounds**, the two rings share only one single atom, the spiro atom, which is usually a quaternary carbone:



spiro [5.4] decane

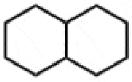


spiro [4.3] octane



spiro [5.2] octane

In **fused bicyclic compounds**, two rings share two adjacent atoms:

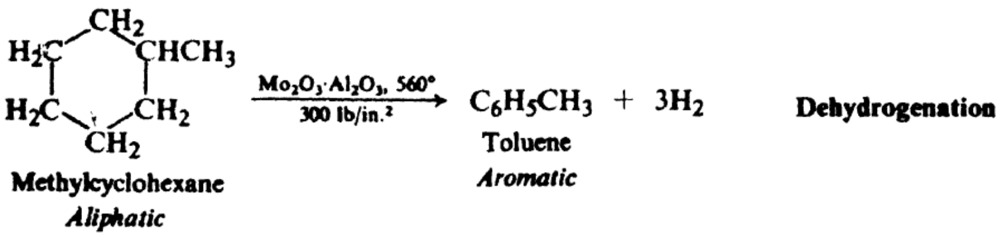


Ten carbon alkane: **decane**
Bridge lengths: 4, 4, 0

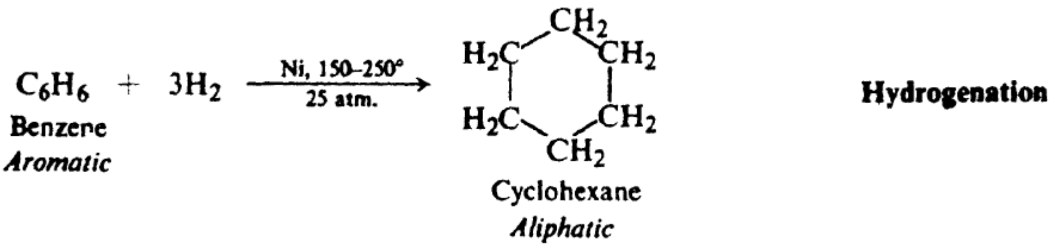
bicyclo[4.4.0]decane

2. Industrial source :

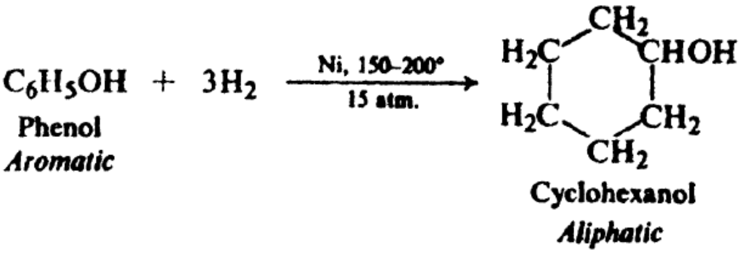
Petroleum from certain areas, (in particular California) is rich in cycloalkanes, known to the petroleum industry as naphthenes. Among these are cyclohexane, methylcyclohexane, methylcyclopentane, and 1,2-dimethylcyclopentane. These cycloalkanes are converted by catalytic reforming into aromatic hydrocarbons, for example:



Just as elimination of hydrogen from cyclic aliphatic compounds yields aromatic compounds, so addition of hydrogen to aromatic compounds yields cyclic aliphatic compounds, specifically cyclohexane derivatives. An important example of this is the hydrogenation of benzene to yield pure cyclohexane:



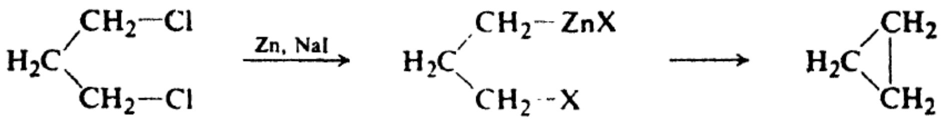
As we might expect, hydrogenation of substituted benzenes yields substituted cyclohexanes. For example:



3. Preparation :

Preparation of alicyclic hydrocarbons from other aliphatic compounds generally involves two stages:

(a) conversion of some open-chain compounds(di halide) into a compound that contains a ring, a process called cyclization:



1,3-Dichloropropane Cyclopropane

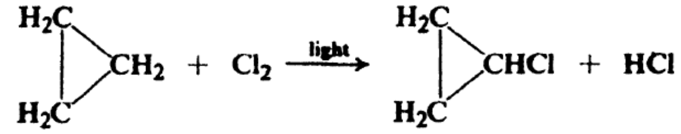
(b) Alicyclic hydrocarbons are prepared from other cyclic compounds, for example, conversion of a cyclic alcohol into a cyclic alkene or of a cyclic alkene into a cyclic alkane.

Problem: Starting with cyclohexanol, how would you prepare: (a) cyclohexene, (b) 3-bromocyclohexene, (c) 1,3-cyclohexadiene?

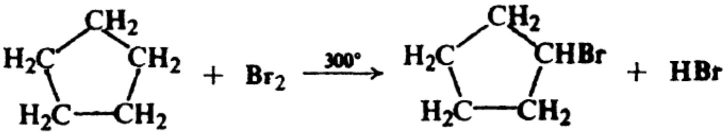
Problem: Bromocyclobutane, How would you prepare cyclobutane from it?

4. Reactions :

Cycloalkanes undergo chiefly free-radical substitution. For example:

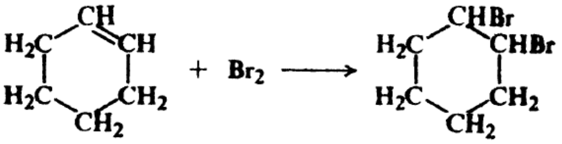


Cyclopropane Chlorocyclopropane

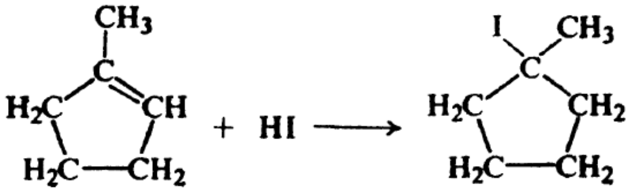


Cyclopentane Bromocyclopentane

Cycloalkenes undergo chiefly addition reactions, both electrophilic and free radical; like other alkenes:

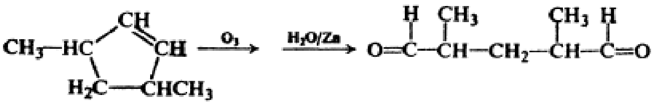


Cyclohexene 1,2-Dibromocyclohexane



1-Methylcyclopentene 1-Iodo-1-methylcyclopentane

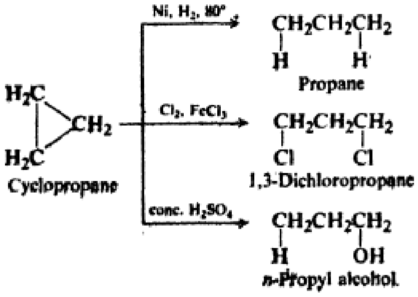
They can also undergo cleavage and allylic substitution. For example:



3,5-Dimethylcyclopentene A dialdehyde

4.1 Reactions of small-ring compounds: Cyclopropane and cyclobutane

Besides the free-radical substitution reactions that are characteristic of cycloalkanes, cyclopropane and cyclobutane undergo certain addition reactions. These addition reactions destroy the cyclopropane and cyclobutane ring system, and yield open-chain products. For example:



Cyclobutane undergo most of the ring-opening reactions of cyclopropane; but only under more vigorous conditions than those required for cyclopropane, thus cyclobutane undergoes addition less readily than cyclopropane.

5. Baeyer strain theory :

Baeyer's argument was essentially the following. In general, when carbon is bonded to four other atoms, the angle between any pair of bonds is the tetrahedral angle 109.5°. But the ring of cyclopropane is a triangle with three angles of 60°, and the ring of cyclobutane is a square with four angles of 90°. In cyclopropane or cyclobutane, therefore, one pair of bonds to each carbon cannot assume the tetrahedral angle, but must be compressed to 60 or 90 to fit the geometry of the ring.

These deviations of bond angles from the "normal" tetrahedral value cause the molecules to be strained, and hence to be unstable compared with molecules in which the bond angles are tetrahedral. Cyclopropane and cyclobutane undergo ring-opening reactions since these relieve the strain and yield the more stable openchain compounds. Because the deviation of the bond angles in cyclopropane (109.5 - 60 = 49.5) is greater than in cyclobutane (109.5 - 90 =19.5), cyclopropane is more highly strained, more unstable, and more prone to undergo ring-opening reactions than is cyclobutane.

The angles of a regular pentagon (108°) are very close to the tetrahedral angle (109.5°), and hence cyclopentane should be virtually free of angle strain. The angles of a regular hexagon (120°) are somewhat larger than the tetrahedral angle, and hence, Baeyer proposed (incorrectly), there should be a certain amount of strain in cyclohexane. Further, he suggested (incorrectly) that as one proceed 4 to cycloheptane, cyclooctane, etc., the deviation of the bond angles from 109.5 would become progressively larger, and the molecules would become progressively more strained.

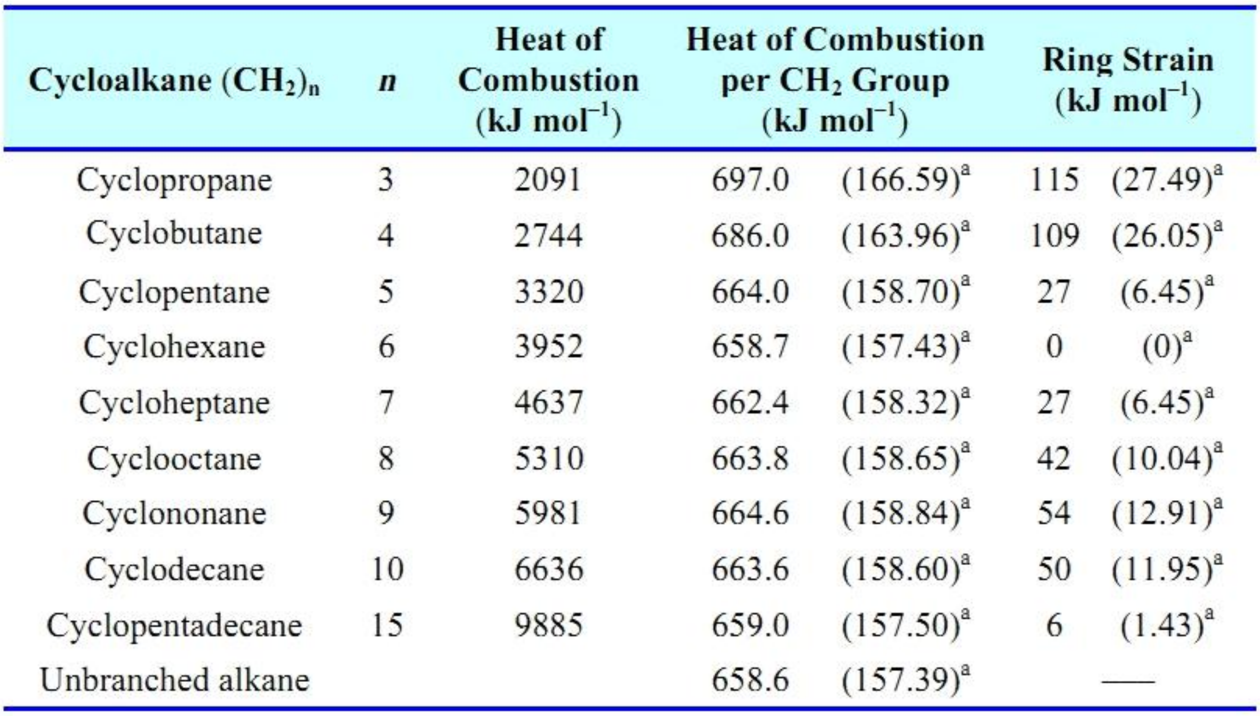
Thus Baeyer considered that rings smaller or larger than cyclopentane or cyclohexane were unstable; it was because of this instability that the three- and four-membered rings underwent ring-opening reactions; it was because of this instability that great difficulty had been encountered in the synthesis of the larger rings. How does Baeyer's strain theory agree with the facts?

6. Heats of combustion and relative stabilities of the cycloalkanes :

The heat of combustion is the quantity of heat evolved when one mole of a compound is burned to carbon dioxide and water. Likes heats of hydrogenation, heats of combustion gives information about the relative stabilities of organic compounds. Let us see if the heats of combustion of the various cycloalkanes support Baeyer's proposal that rings smaller or larger than cyclopentane and cyplohexane are unstable.

For open-chain alkanes each methylene group, CH_2 , contributes very close to 157.4 kcal/mole to the heat of combustion. The following table lists the heats of combustion that have been measured for some of the cycloalkanes:

$$(CH_2)_n + \frac{3}{2} n\, O_2 \longrightarrow n\, CO_2 + n\, H_2O + \text{heat}$$



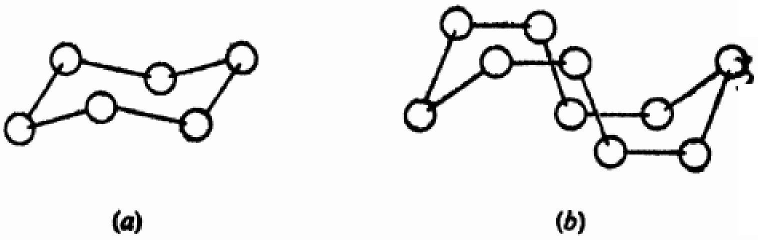
Cycloalkane $(CH_2)_n$	*n*	Heat of Combustion (kJ mol^{-1})	Heat of Combustion per CH_2 Group (kJ mol^{-1})		Ring Strain (kJ mol^{-1})	
Cyclopropane	3	2091	697.0	(166.59)[a]	115	(27.49)[a]
Cyclobutane	4	2744	686.0	(163.96)[a]	109	(26.05)[a]
Cyclopentane	5	3320	664.0	(158.70)[a]	27	(6.45)[a]
Cyclohexane	6	3952	658.7	(157.43)[a]	0	(0)[a]
Cycloheptane	7	4637	662.4	(158.32)[a]	27	(6.45)[a]
Cyclooctane	8	5310	663.8	(158.65)[a]	42	(10.04)[a]
Cyclononane	9	5981	664.6	(158.84)[a]	54	(12.91)[a]
Cyclodecane	10	6636	663.6	(158.60)[a]	50	(11.95)[a]
Cyclopentadecane	15	9885	659.0	(157.50)[a]	6	(1.43)[a]
Unbranched alkane			658.6	(157.39)[a]	——	

[a] In kcal mol^{-1}.

Cyclopropane and cyclobutane evolve more energy per CH_2 group than an open-chain compound, it can mean only that they contain more energy per (CH_2) group. In agreement with the Baeyer angle-strain theory, then, cyclopropane and cyclobutane are less stable than open-chain compounds; it is reasonable to suppose that their tendency to undergo ring-opening reactions is related to this instability. According to Baeyer, rings larger than cyclopentane and cyclohexane also should be unstable, and hence also should have high heats of combustion; further more relative instability and, with it, heat of combustion should increase steadily with ring size.

However, we see from above table that almost exactly the opposite is true. For none of the rings larger than four carbons does the heat of combustion per CH_2 deviate much from the open-chain value of 157.4. Indeed, one of the biggest deviations is for Baeyer's "most stable" compound, cyclopentane: 1.3 kcal per CH_2 , or 6.5 kcal for the molecule. Rings containing seven to eleven carbons have about the same value as cyclopentane, and when we reach rings of twelve carbons or more, heats of combustion are indistinguishable from the open chain Values. Contrary to Baeyer's theory, then, none of these rings is appreciably less stable than open-chain compounds, and the larger ones are completely free of strain. Furthermore, once they have been synthesized, these large-ring cycloalkanes show little tendency to undergo the ring-opening reactions characteristic of cyclopropane and cyclobutane.

What is wrong with Baeyer's theory that it does not apply to rings larger than four members? Simply this: the angles that Baeyer used for each ring were based on the assumption that the rings were flat. For example, the angles of a regular (flat) hexagon are 120, but the cyclohexane ring is not a regular hexagon, this ring is not flat, but is puckered so that each bond angle of carbon can be 109.5°:



Puckered rings. (*a*) Cyclohexane. (*b*) Cyclodecane.

A three-membered ring must be planar, A four membered ring need not be planar, but puckering.

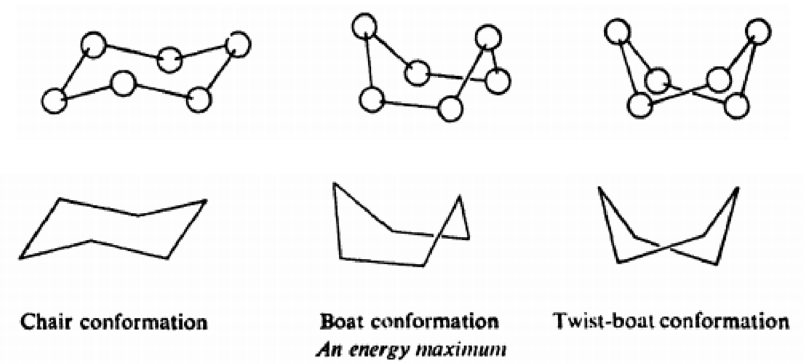
7. Factors affecting stability of conformations:

1) Any atom tends to have bond angles: tetrahedral (109.5) for sp3-hybridized carbon, any deviations from the "normal" bond angles are accompanied by **angle strain**.
2) Any pair of tetrahedral carbons attached to each other tend to have their bonds staggered. like ethane, to take up a staggered conformation. Any deviations from the staggered arrangement are accompanied by **torsional strain**.
3) Non-bonded interactions can be either destabilization or stabilization of the conformation. If brought any closer together, they repel each other: such crowding together is accompanied by **van der Waals strain (steric strain)**.
4) dipole-dipole repulsions or maximize dipole-dipole attractions. A particularly powerful attraction results from the special kind of dipole-dipole interaction called the **hydrogen bond**.

All these factors, working together or opposing each other, determine the net stability of a conformation.

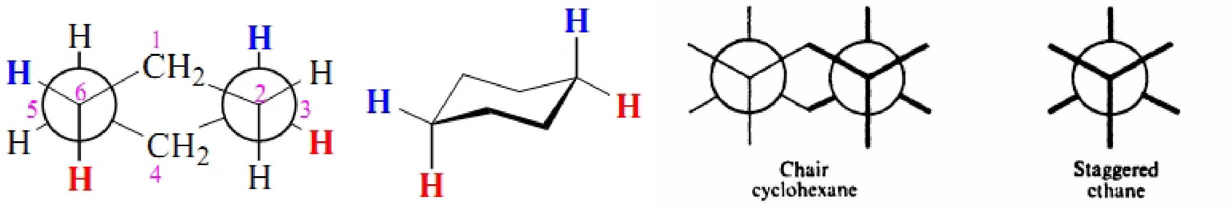
8. Conformations of cycloalkanes :

Starting with cyclohexane (the most important of the cycloalkanes) as a model of the molecule, and examine the conformations that are free of angle strain:


Chair conformation
Boat conformation
An energy maximum
Twist-boat conformation

Conformations of cyclohexane that are free of angle strain.

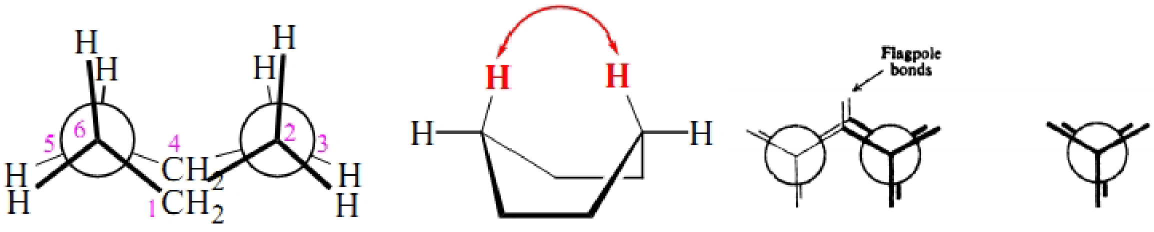
The chair form: each of the carbon-carbon bonds are perfectly staggered bonds:



A Newman projection of the chair conformation of cyclohexane.

The conformation is thus not only free of angle strain but free of torsional strain. The chair form is the most stable conformation of cyclohexane.

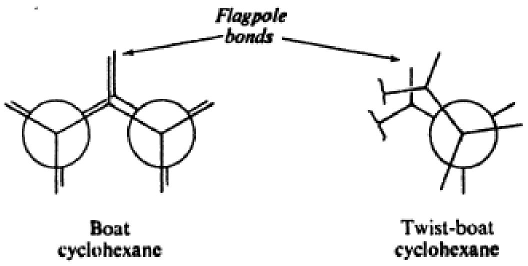
The boat conformation: This is not a very happy arrangement, we see sets of exactly eclipsed bonds:



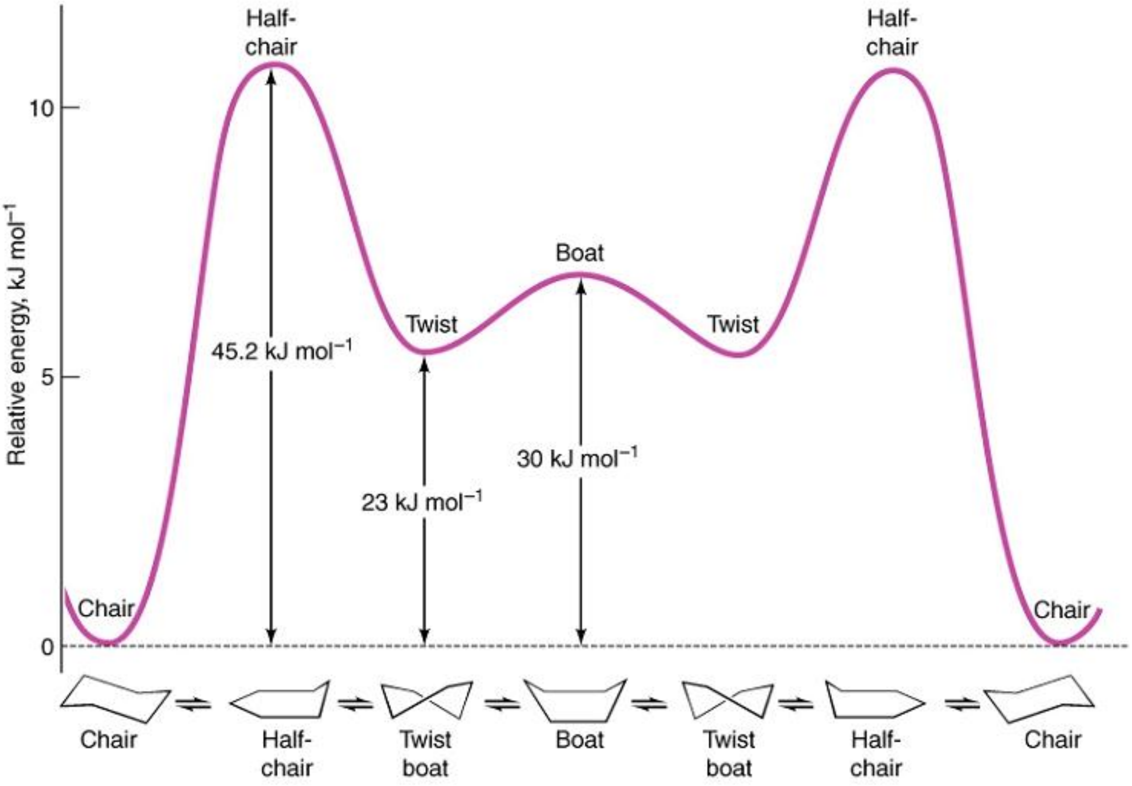
the eclipsed conformation of the boat conformation

and hence we expect considerable torsional strain: as much as in two ethane molecules. In addition, there is van der Waals strain due to crowding between the "flagpole" hydrogens. The boat conformation is less stable than the chair conformation. It is an energy maximum; it is a transition state between two conformers, chair and twist-boat conformations.

This new configuration is the twist-boat form, lying at energy minimum 5.5 kcal above the chair conformation. The twist-boat conformed is separated from another, enantiomeric twist-boat conformer by an energy barrier 1.6 kcal high, at the top of which is the boat conformation:

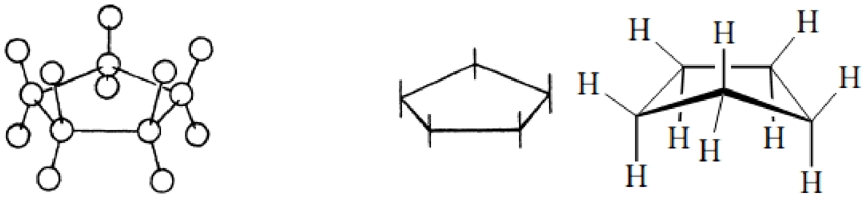


Between the chair form and the twist-boat forth lies the highest barrier of all; a transition state conformation (the half-chair) which, with angle strain and torsional strain, lies about 11 kcal above the chair form.



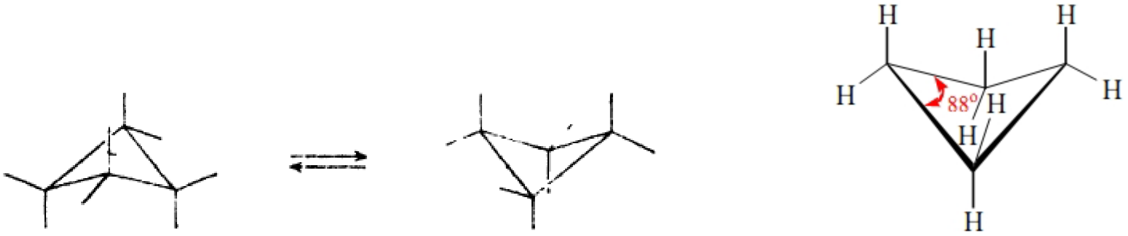
The relative energies of the various conformations of cyclohexane.

Planar **cyclopentane** exact bond eclipsing between every pair of carbons. To (partially) relieve this torsional strain, cyclopentane takes on a slightly puckered conformation, even at the cost of a little angle strain:



Planar cyclopentane: much torsional strain. Molecule actually puckered.

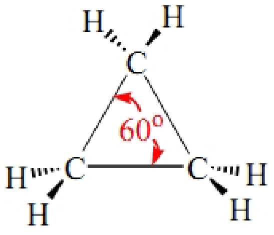
Evidence indicates that cyclobutane is not planar, but rapidly changes between equivalent, slightly folded conformations. Here, too, torsional strain is partially relieved at the cost of a little angle strain:

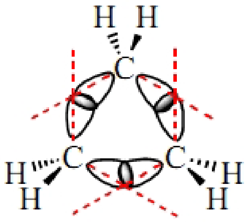


Cyclobutane: rapid transformation between equivalent nonplanar "folded" conformations.

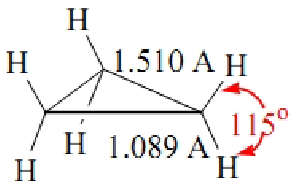
8.1 THE ORIGIN OF RING STRAIN IN CYCLOPROPANE

The carbon atoms of alkanes are *sp*3 hybridized ⇨ the bond angle is 109.5°. The internal angle of cyclopropane is 60° and departs from the ideal value by a very large amout — by 49.5°.

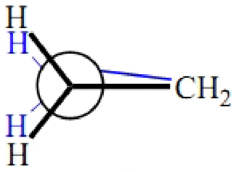




angle strain



Bond distances and angles in cyclopropane



eclipsed hydrogens

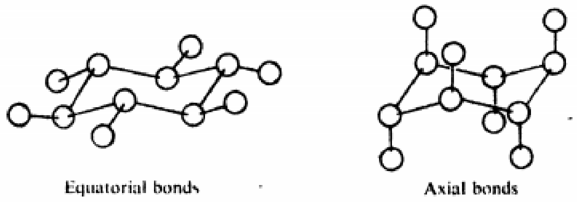
The **C—C bonds** of cyclopropane are "**bent**" ⇨ **orbital overlap is less effectively** (the orbitals used for these bonds are not purely *sp*3, they contain more *p* character) ⇨ the **C—C bonds** of cyclopropane are **weaker** ⇨ cyclopropane has greater potential energy.

The hydrogen atoms of the cyclopropane ring are all **eclipsed** ⇨ cyclopropane has **torsional strain**.

Rings containing seven to twelve carbon atoms are also subject to torsional strain, and hence these compounds, are less stable than cyclohexane; scale models also reveal serious crowding of hydrogens inside these rings.

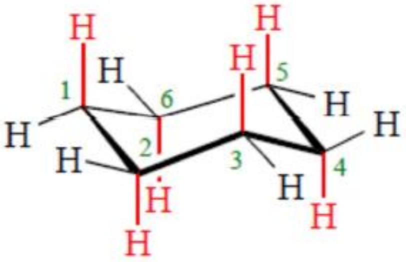
8.1 Equatorial and axial bonds in cyclohexane :

Let us return to the model of the chair conformation of cyclohexane. Although the cyclohexane ring is not flat, we see that the hydrogen atoms occupy two kinds of position: six hydrogens lie in the plane called **equatorial**, while six hydrogens lie above or below the plane called **axial**:

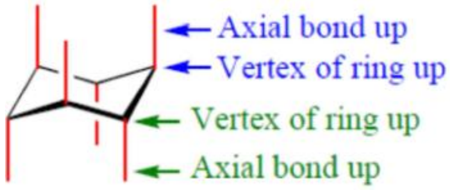

Equatorial bonds

Axial bonds

Figure 9.8. Equatorial and axial bonds in cyclohexane.



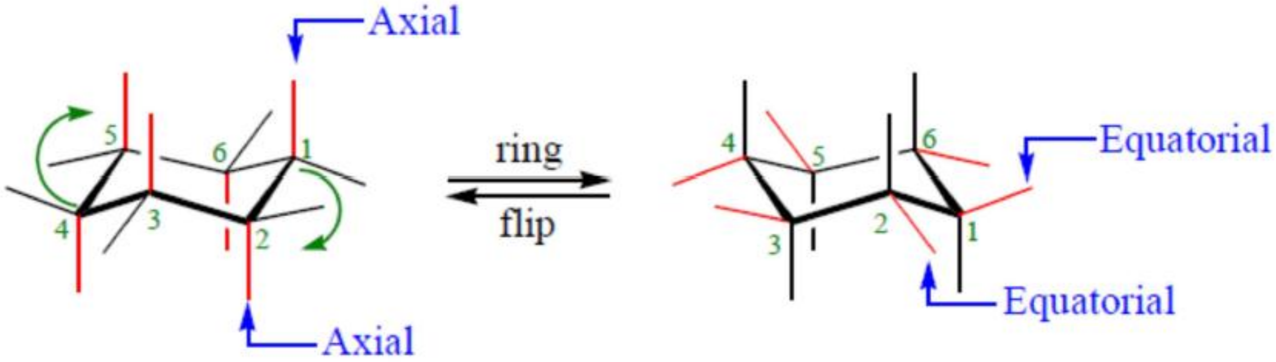
Sets of parallel lines that constitute the ring and equatorial C–H bonds of the chair conformation.



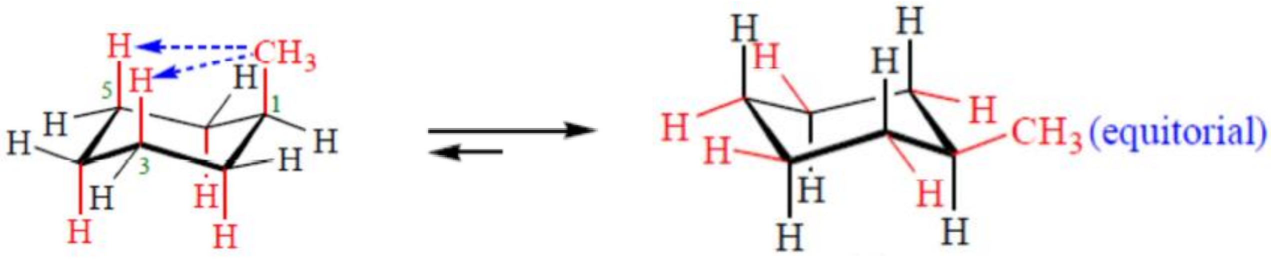
The axial bonds are all vertical. When the vertex of the ring points up, the axial bond is up and vice versa.

Ring flip:

When the ring flips, all of the bonds that were axial become equatorial and vice versa.



There are two possible chair conformations of methylcyclohexane.

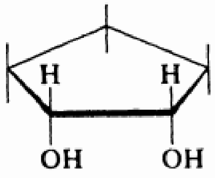


(less stable) **(Less crowding, more stable by 7.5 KJ mole^{-1})**

The strain caused by a 1,3-diaxial interaction van der Waals forces between them are repulsive.

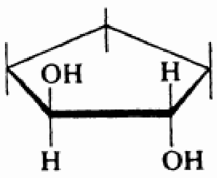
9. Stereoisomerism of cyclic compounds:

We shall begin with the glycol of cyclopentane, 1,2-cyclopentanediol. Using models, we find that we can arrange the atoms of this molecule as in I, in which both hydroxyls lie below (or above) the plane of the ring, and as in II, in which one hydroxyl lies above and the other lies below the plane of the ring:



I

cis-1,2-Cyclopentanediol

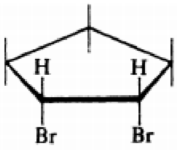


II

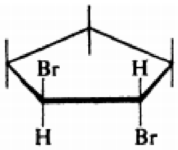
trans-1,2-Cyclopentanediol

The physical properties of *cis-trans* isomers are different: they have different **melting points**, **boiling points**, and so on.

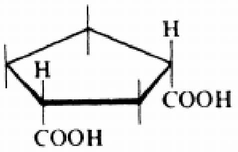
Some examples of isomers that have been isolated are:



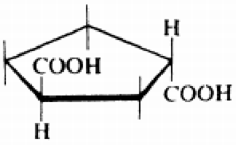
cis-1,2-Dibromocyclopentane



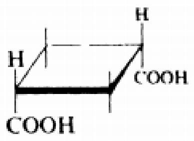
trans-1,2-Dibromocyclopentane



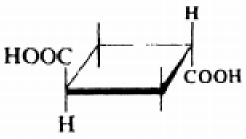
cis-1,3-Cyclopentanedicarboxylic acid



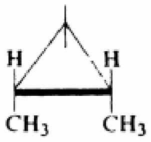
trans-1,3-Cyclopentanedicarboxyli acid



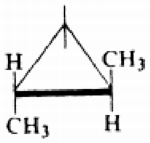
cis-1,3-Cyclobutanedicarboxylic acid



trans-1,3-Cyclobutanedicarboxylic acid



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

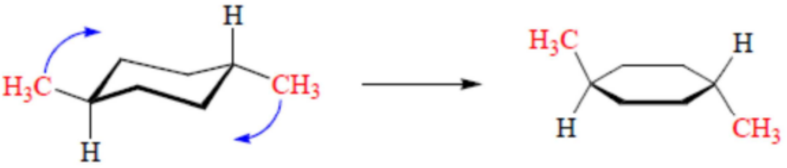
Problem: Draw structural formulas for all stereoisomers of the following:

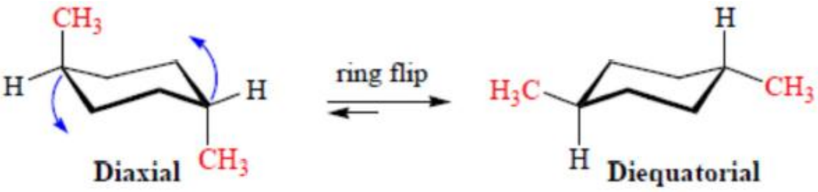
(a) cis-2-chlorocyclohexanol (b) trans-3-chlorocyclopentanol

(c) trans-2-chlorocyclohexanol

10 CIS-TRANS ISOMERISM AND CONFORMATIONAL STRUCTURES:

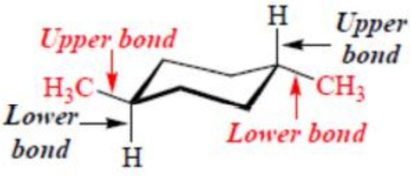
There are two possible chair conformations of *trans*-1,4-dimethylcyclohexane:



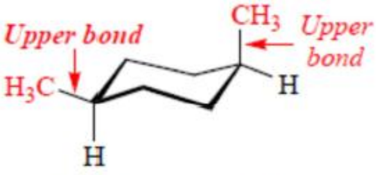


1) **Diaxial** and **diequatorial** *trans*-1,4-dimethylcyclohexane.
2) The **diequatorial** conformation is the **more stable** conformer and it represents at least **99%** of the molecules at equilibrium.

In a ***trans*-disubstituted** cyclohexane, one group is attached by an ***upper*** bond and one by the ***lower*** bond; in a ***cis*-disubstituted** cyclohexane, both groups are attached by an ***upper*** bond or both by the ***lower*** bond.

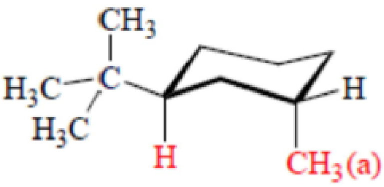


trans-1,4-Dimethylcyclohexane



cis-1,4-Dimethylcyclohexane

trans-1,3-Disubstituted cyclohexane with two **different alkyl groups**, the conformation of **lower energy** is the one having the **larger group** in the **equatorial** position.



Conformations of Dimethylcyclohexanes

Compound	*Cis* Isomer	*Trans* Isomer
1,2-Dimethyl	*a,e* or *e,a*	*e,e* or *a,a*
1,3-Dimethyl	*e,e* or *a,a*	*a,e* or *e,a*
1,4-Dimethyl	*a,e* or *e,a*	*e,e* or *a,a*