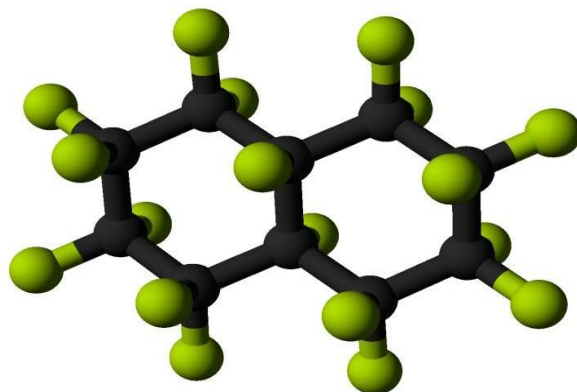


CONFORMATIONAL ANALYSIS OF DECALINS & BRIDGE RING COMPOUNDS



Conformations

❖ The infinite number of arrangements of the atoms or groups of a molecule in three dimensional space which are interconvertible into each other by rotation about single bond are called **Conformations** or **Rotational Isomers** or simply **Rotamers**.

❖ These conformers have different internal dimensions (atom-to-atom distances, dihedral angles, dipole moment etc.)

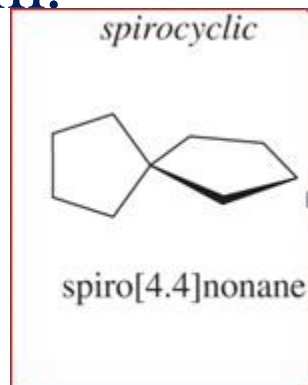
.

❖ The energy barrier for rotation of carbon-carbon single bonds (conversion of different spatial arrangements) is normally small, < 0.6 kcal/mol and > 16 kcal/mol.

Conformation of Bicyclic Compounds

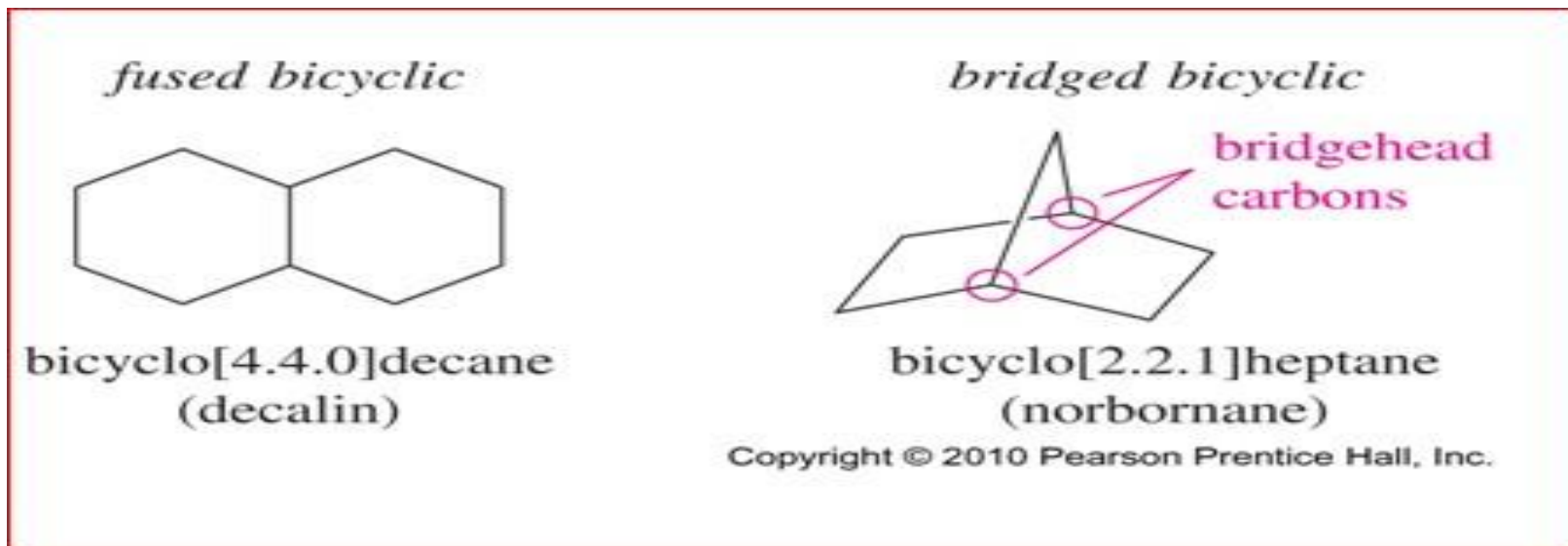
Compounds with two or more rings fused together

- **Spirocyclic:** -Two or more rings.
 - Each pair of rings shares one common carbon atom.



- **Bicyclic:** Two rings that share two or more common atoms

A Bicyclic system can be further Fused and Bridged bicyclic.

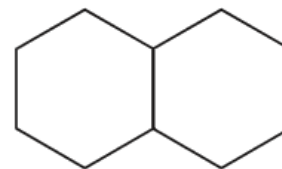


Fused rings share two adjacent carbon atoms and the bond between them

These share two non-adjacent carbon atoms (the bridgehead carbons) and one or more carbon atoms between them.

Conformation of Decalin

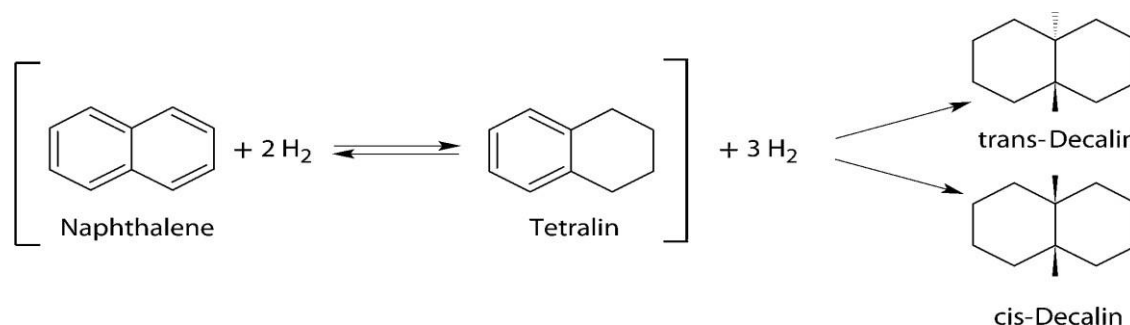
(Decahydronaphthalene)



decalin
(bicyclo[4.4.0]decane)

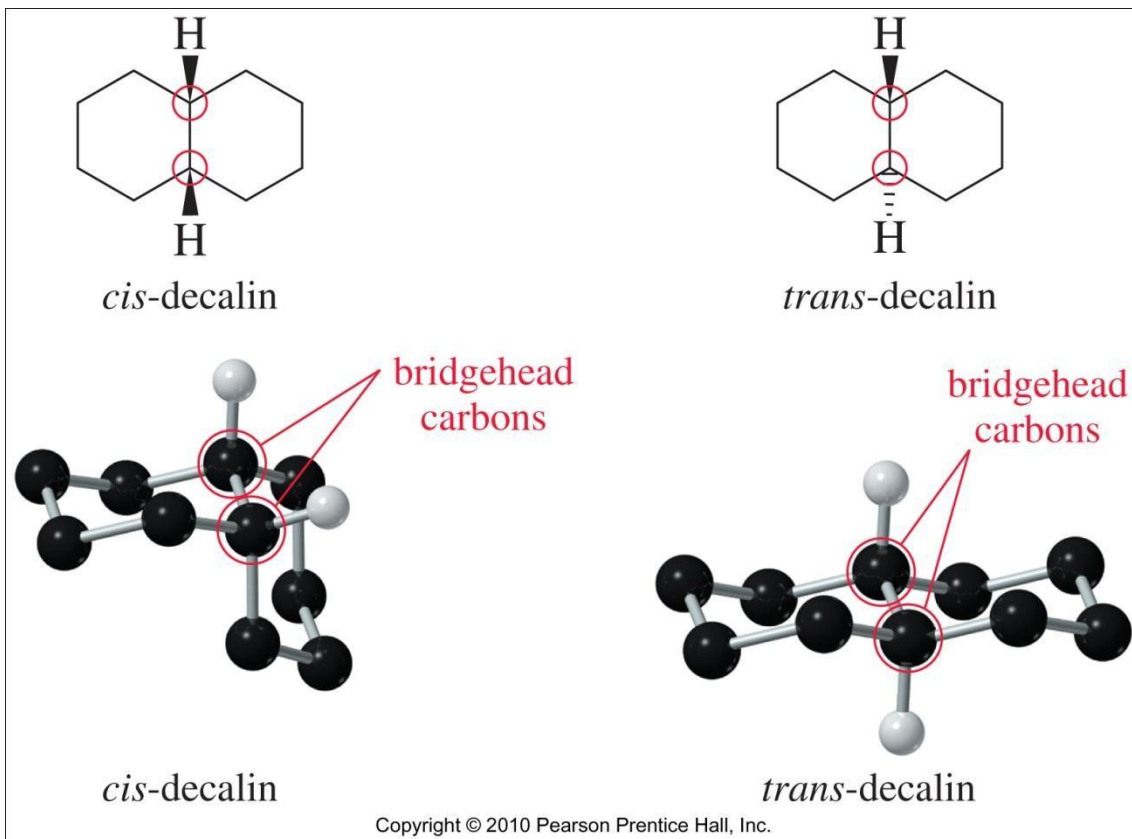
❖ Fused Bicyclic system

❖ Saturated analogue of naphthalene and can be prepared from it by hydrogenation in a fused state in the presence of a catalyst



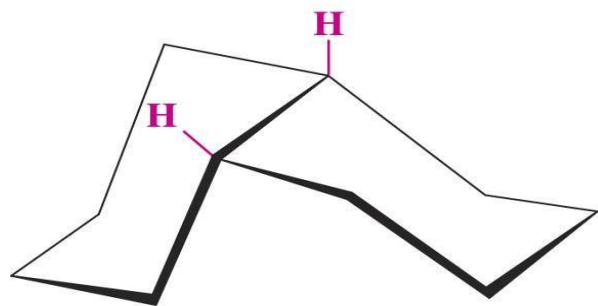
❖ Sachse-Mohr proposed decalin is a puckered strain-free two rings cycloalkane, existed in two forms that could interconvert only by breaking and reforming bonds.

In 1925, Walter Hückel isolated the two postulated isomers of decalin.

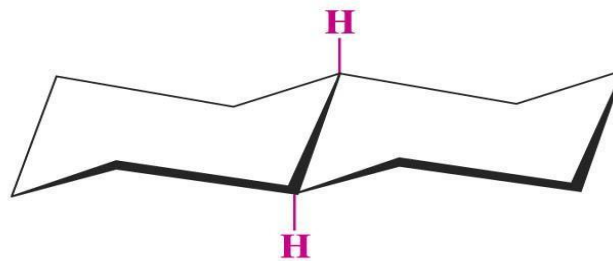


Decalin is a hydrocarbon which has six-membered rings like those of cyclohexane, are expected to be most stable in the chair form.

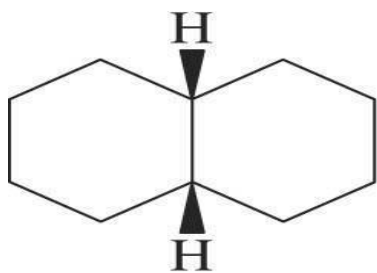
However, there are two possible ways in which two chairs conformations of cyclohexane can be joined.



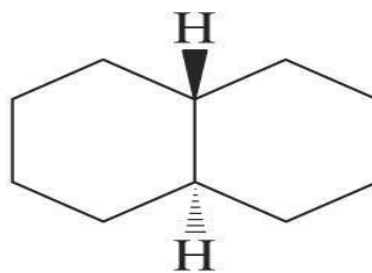
cis-Decalin



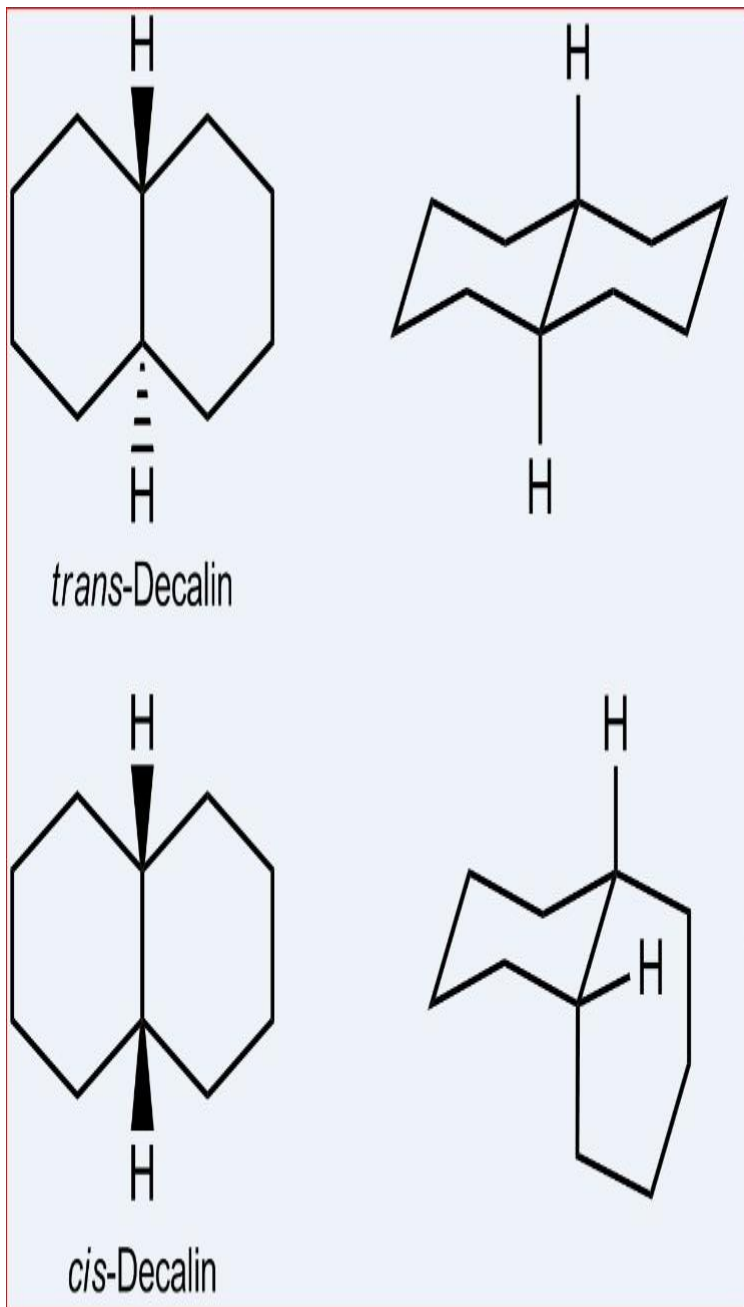
trans-Decalin



cis-Decalin



trans-Decalin

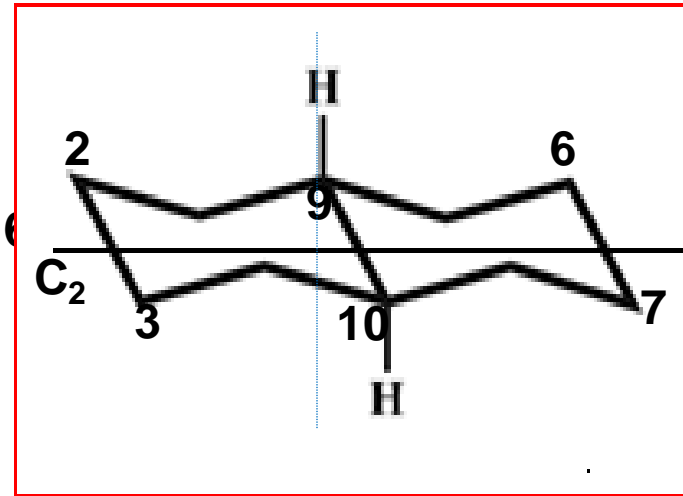


Each chair is fused to the other by equatorial bonds, leaving the angular hydrogens (H_a) axial to both rings. The hydrogens on the ring junction carbons are **trans** in this diastereomer

Chair conformations the rings are fused by one axial and one equatorial bond and the overall structure is bent at the ring fusion. (C-1 axial, C-6 equatorial) The hydrogens on the ring junction carbons are **cis** to each other.

Symmetry

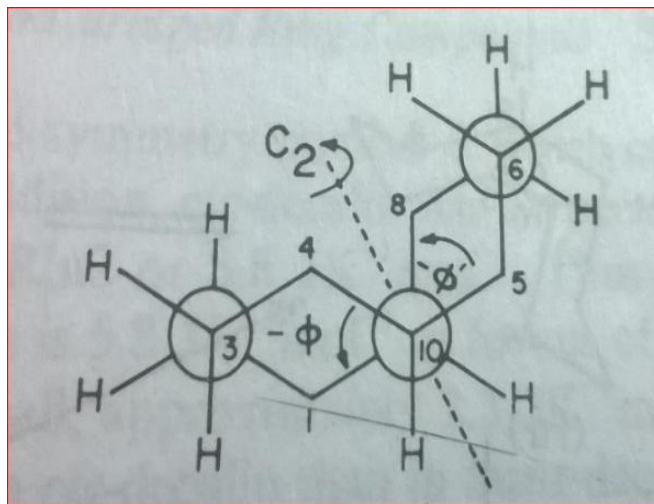
trans-decalin



- Conformationally locked frame work.
- No undergo ring inversion.
- Achiral.
- Center of symmetry (mid-point of the 9-10 bond)
- C₂ axis passing between C-2 and C-3, C-9 and C-10, and C-6 and C-7

Symmetry

cis-decalin:



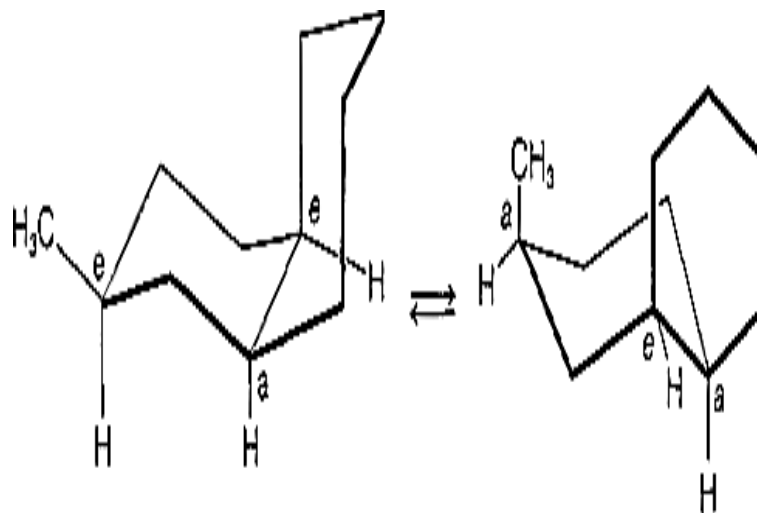
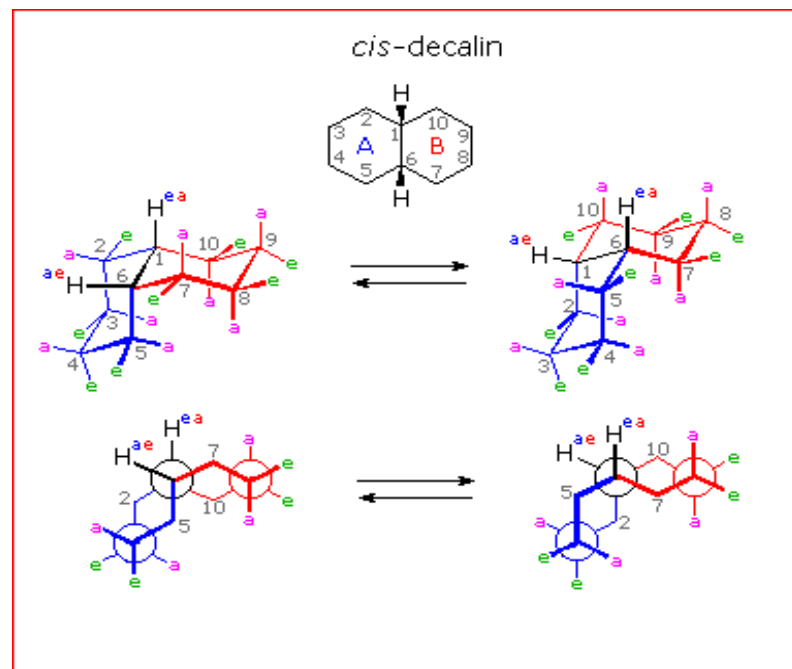
- Cis isomer is chiral without chiral center.
- Two-fold rotational symmetry axis going through the center of 1-6 bond but no reflective symmetry.
- However, the chirality is cancelled through a rapid chair flipping process that turns the molecule into its mirror image. Hence that compound is not resolvable.
- Has a folded structure with a convex and a concave side so that the steric interactions are unequally distributed on the two sides

Ring flipping / Ring Inversion

cis-decalin:

❖ Each ring in cis-decalin can undergo ring flip forming two different chair-chair conformations of equal energy.

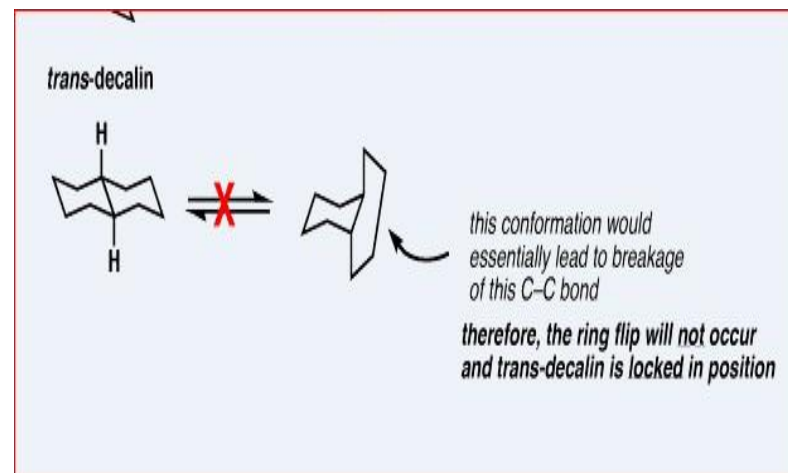
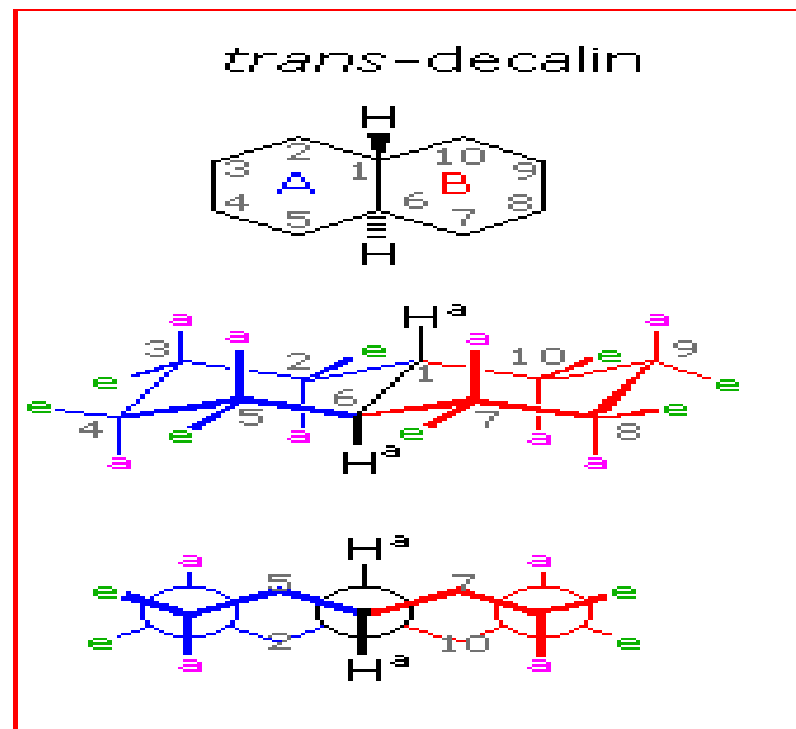
❖ Each of the angular hydrogens is oriented axial to one of the rings and equatorial to the other. This relationship reverses when double ring flipping converts one cis-conformer into the other.

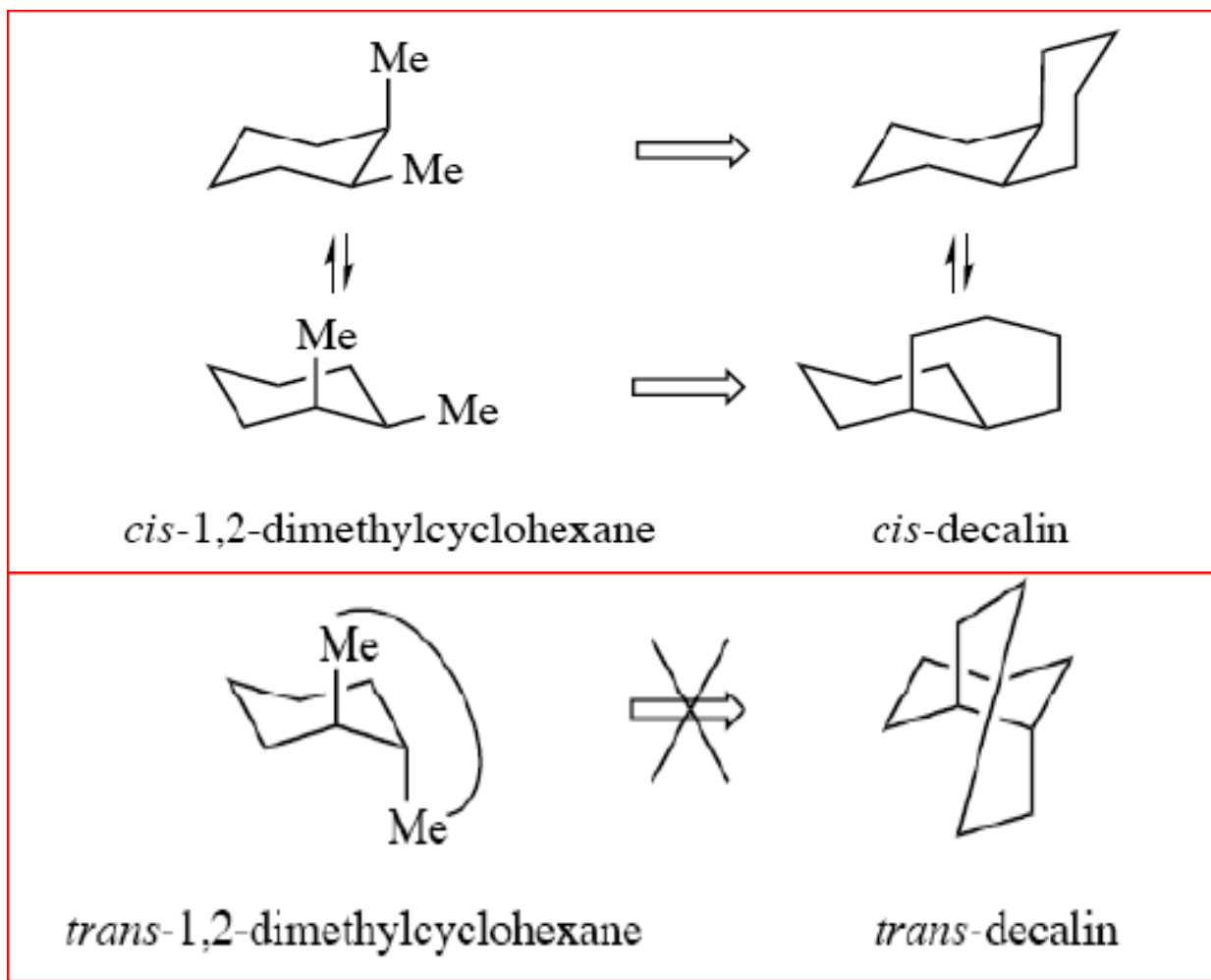


trans-decalin:

❖ trans-decalin is incapable of ring flipping, because a ring flip of one ring would cause its two alkyl substituents (which comprise the second ring) to be too far apart to accommodate the second ring.

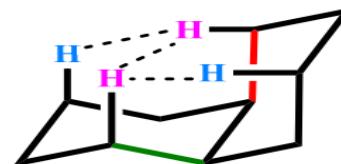
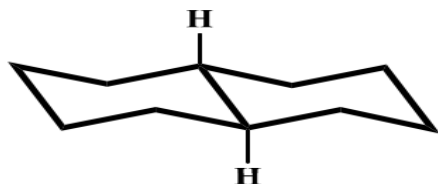
❖ CH_2CH_2 group is insufficiently long to bridge them. trans-Decalin is said to be conformationally locked because it can't undergo a ring flip.





trans-decalin is more stable than *cis*-decalin by 2.7 kcal/mol (11.3 kJ/mol).

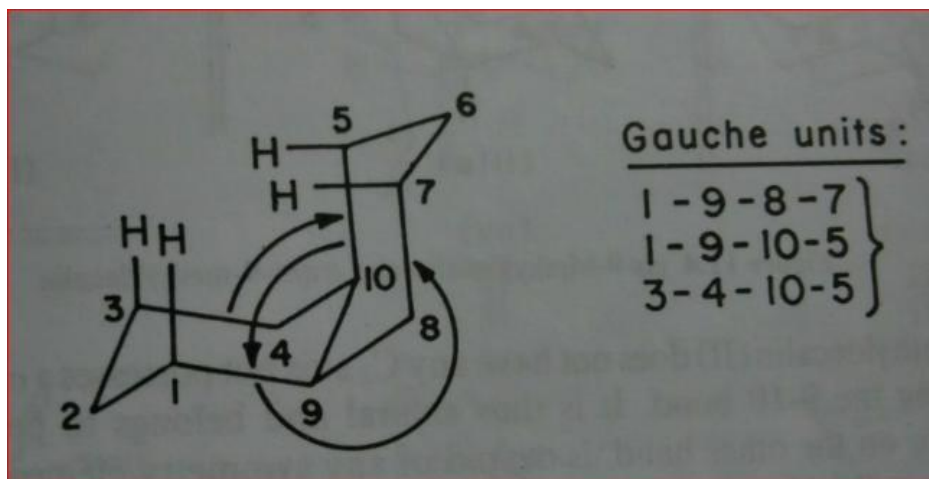
cis Vs trans-Decalin



trans-Decalin is more stable than *cis*-decalin by $3 \times 0.9 = 2.7$ kcal/mol

- ❖ trans isomer is about 2.7 kcal /mole more stable than the cis isomer, largely because of relatively unfavorable nonbonded interactions within the concave area of cis-decalin
- ❖ The small difference in the entropies of the cis – and trans- isomes also suggests the more stability of trans - decalin

❖ No Gauche unit exists in trans-decalin

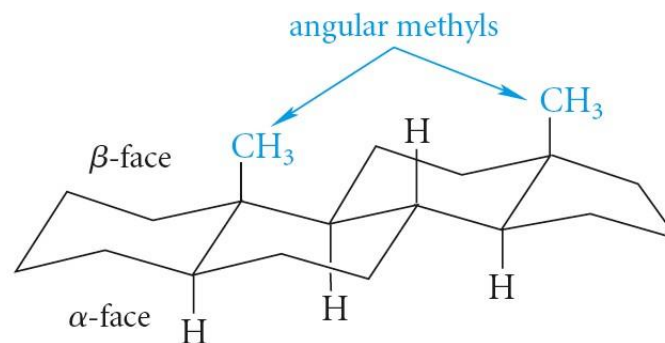
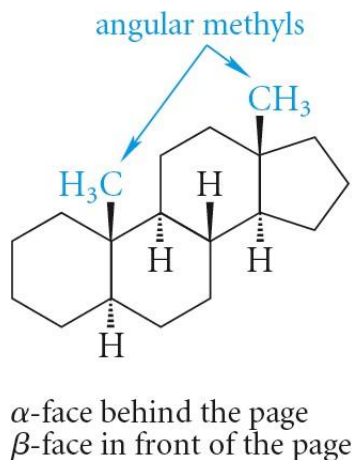


Gauche butane interactions in cis-butane

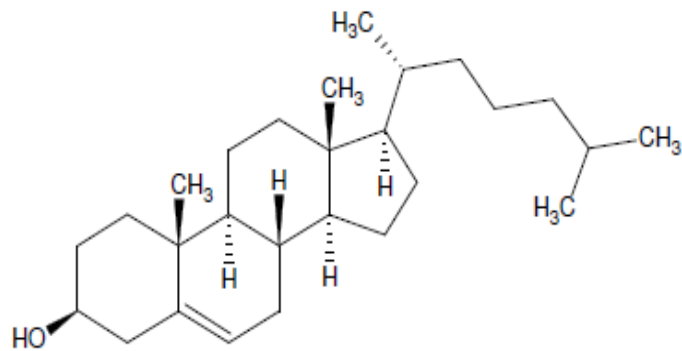
❖ In cis-decalin, three Gauche interactions exist.

❖ The difference in enthalpies is therefore equal to the three gauche interactions (10.05 kJ/mole) (experimental value 8.8-14.2 kJ/mole,)

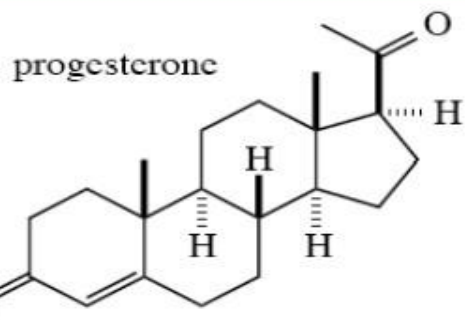
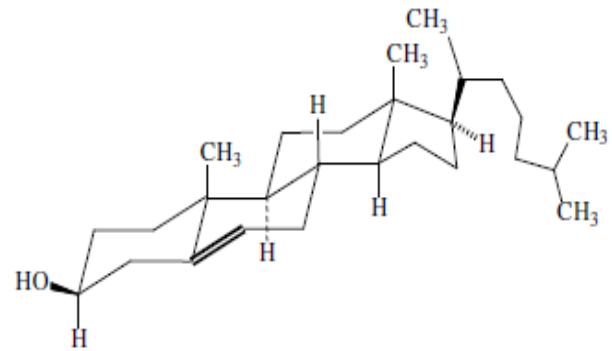
Decaline unit in Steroids



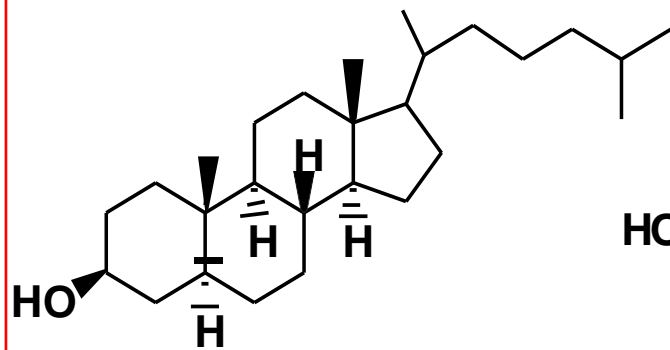
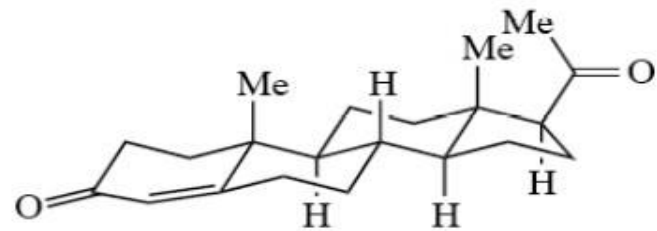
- ❖ Fundamental framework of steroids is a tetracyclic carbon framework.
- ❖ Trans-decalin style fused cyclohexane rings are the basis for steroids.
- ❖ Many have methyl groups at C-10 and C-13



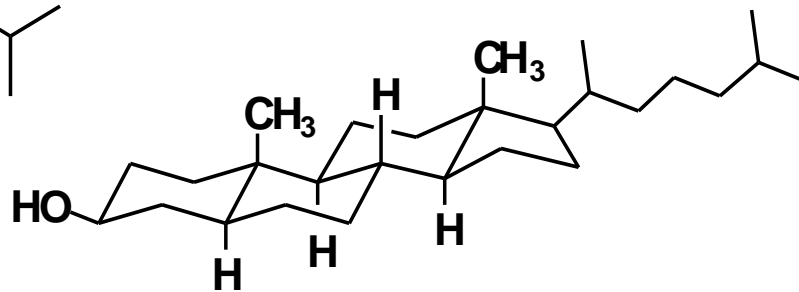
Cholesterol



progesterone

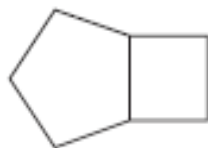


Cholestanol

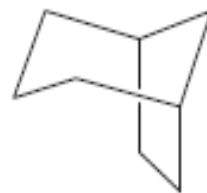


Bridged Ring Compounds

In a bridged bicyclic compound, two rings share two carbon atoms and these carbon atoms are not adjacent.

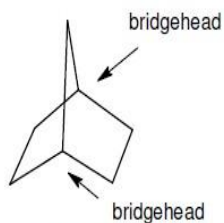


Bicyclo[3.2.0]heptane



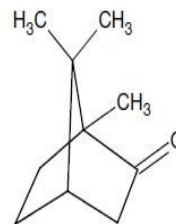
Bicyclo[3.2.1]octane

Bicyclics

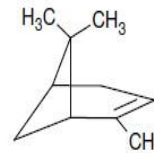


Norbornane

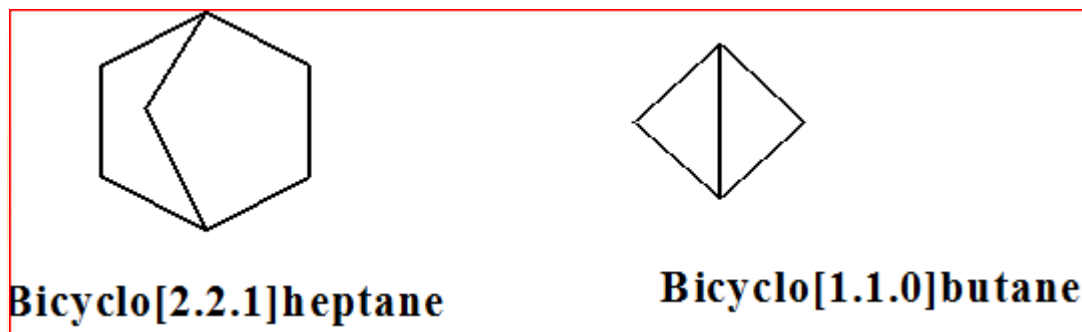
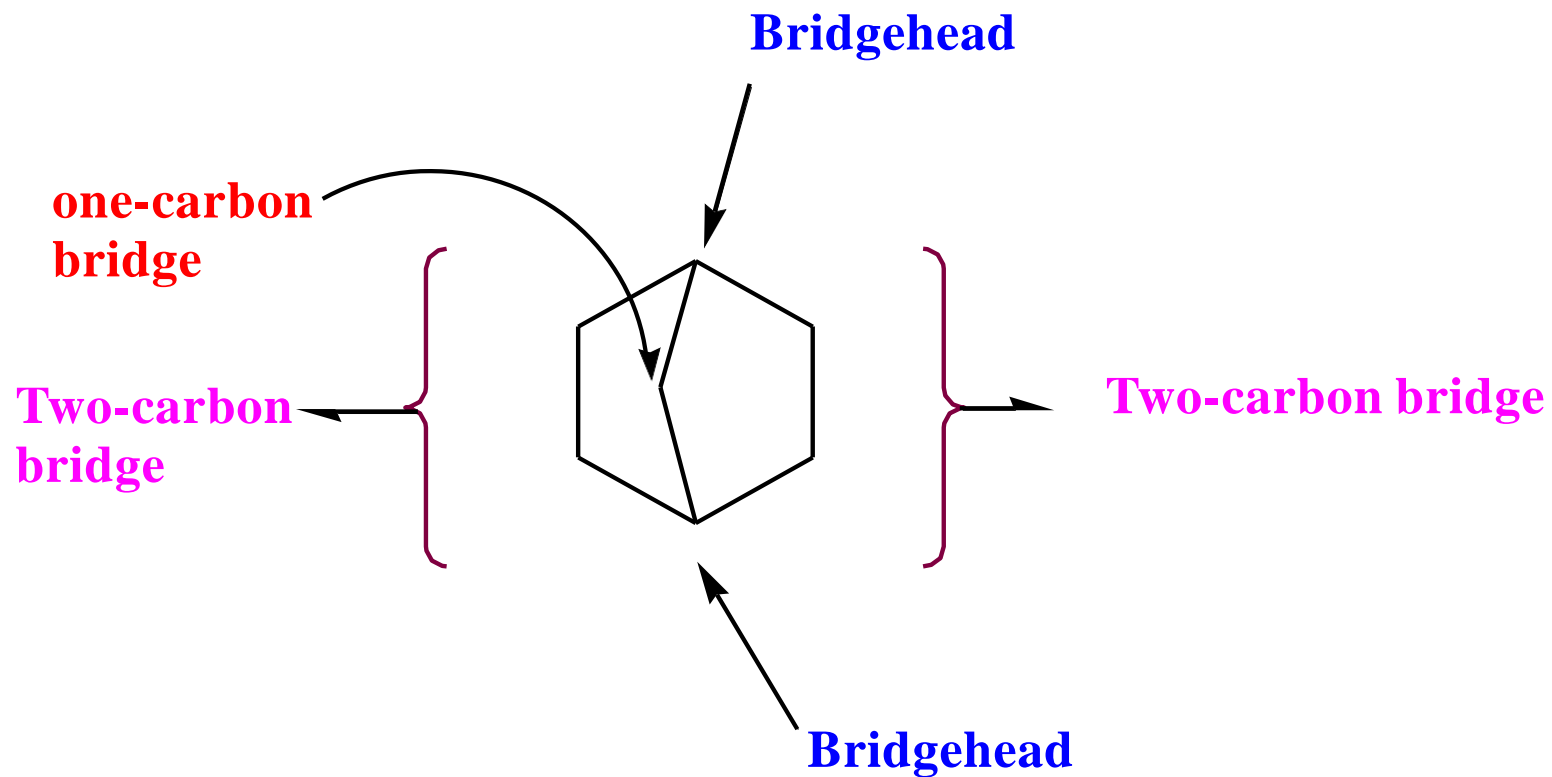
Bicyclo[2.2.1]heptane



camphor

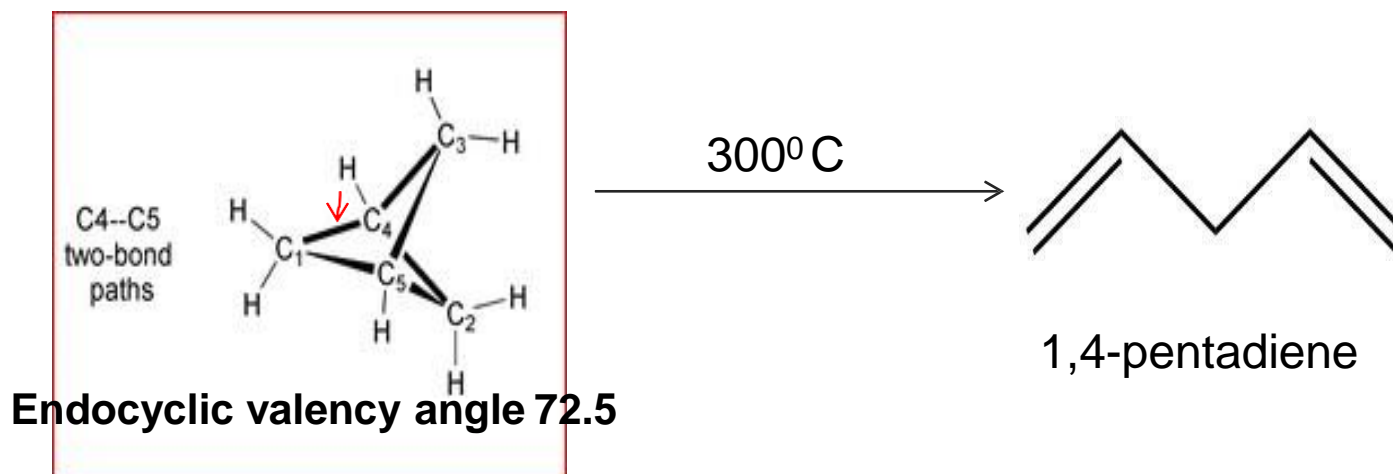


alpha-pinene

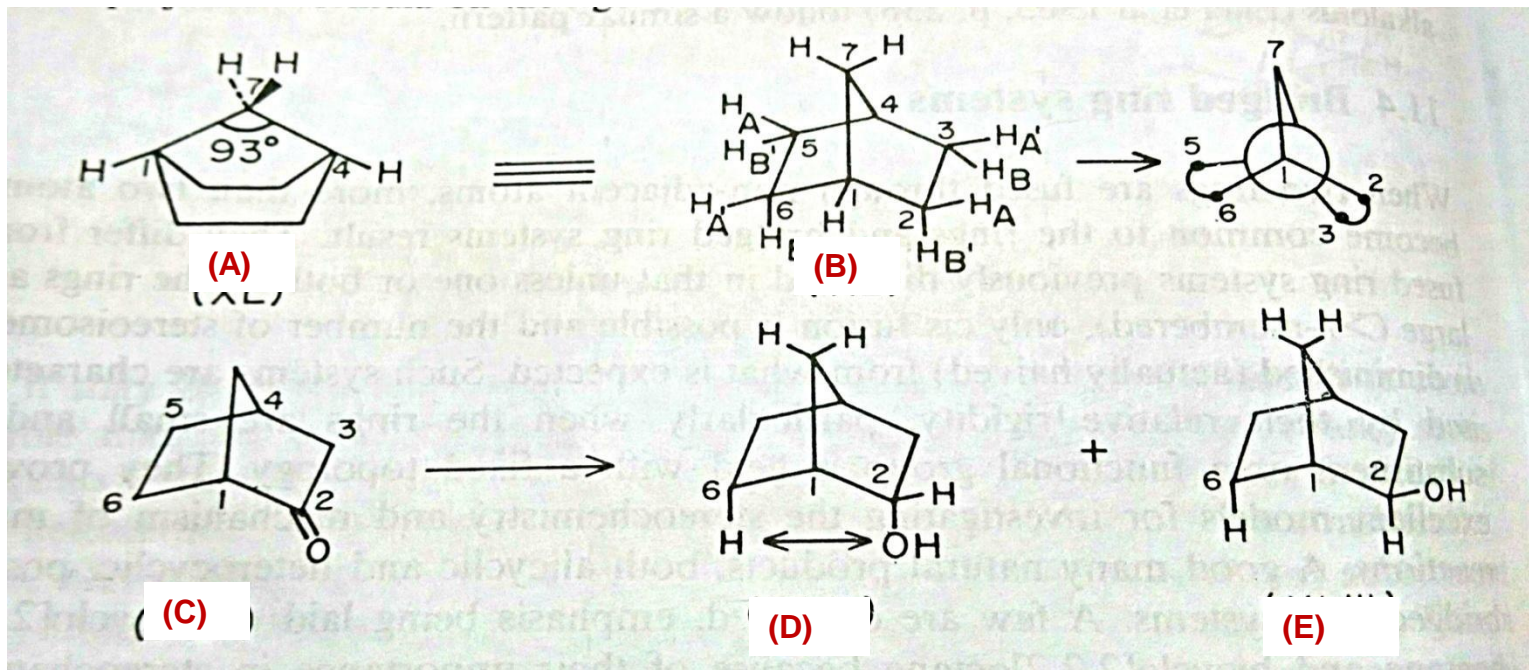


Bicyclo [1.1.1] pentane

- ❖ Smallest bridge ring system
- ❖ Bridged head C are very close due to very small endocyclic valency angle i.e..72.5 °
- ❖ Unstable and converts to 1,4 pentadiene on heating.

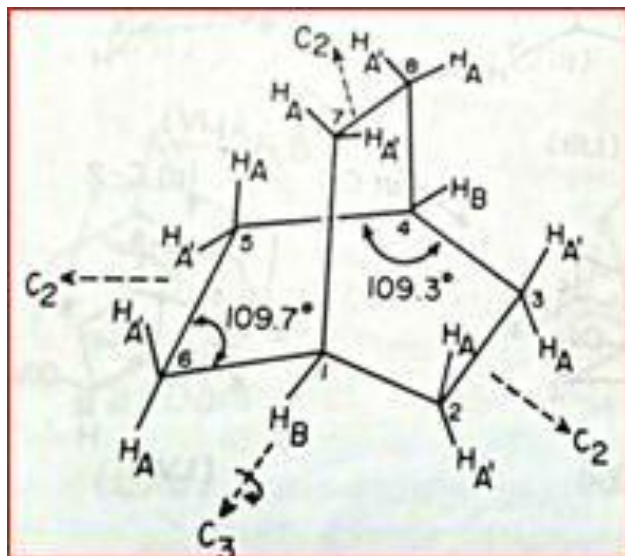


Bicyclo [2.2.1] heptane (Norborane)



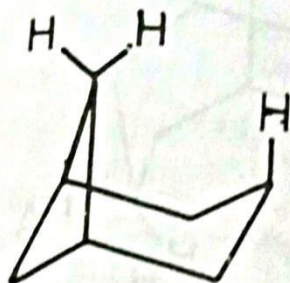
- ❖ C-1 & C-4 are joined by methylene bridge to give boat conformation.
- ❖ System is strained because of two eclipsed butane units in boat.
- ❖ Out of the 6 H's at C-2, C-3, C-5, C-6
 - HA, HA' - boat – equatorial orientation
 - HB, HB' - boat – axial orientation

Bicyclo [2.2.2] octane

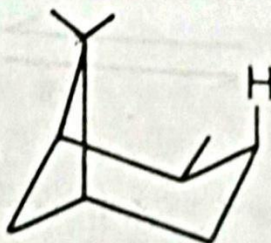


- ❖ C-1 & C-4 are joined by ethylene bridge.
- ❖ In its idealized form the system has all the adjacent positions eclipsed.

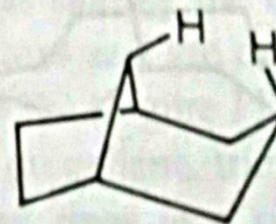
Other Bridge Ring Systems



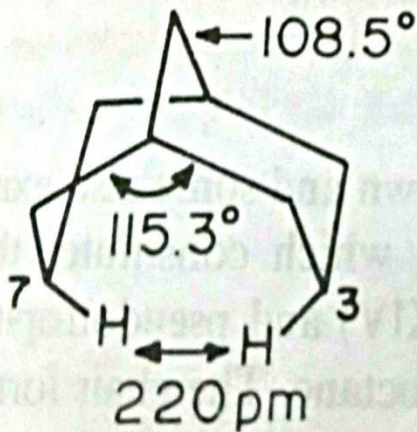
Bicyclo[3.1.1]heptane



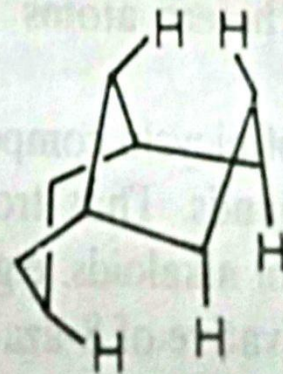
3-Methyl Bicyclo[3.1.1]heptane



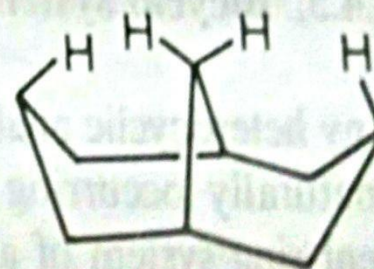
Bicyclo[3.2.1]octane



Bicyclo[3.3.1]nonane
Chair-chair
conformation



Bicyclo[3.3.1]nonane
Boat-chair
conformation



Bicyclo[3.3.1]nonane
Boat-boat conformation

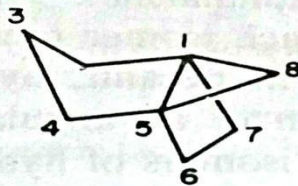
Propellanes & Admantane

When the two bridgehead atoms are joined by a single bond, a tricyclic system is formed where the three rings share two bridgehead atoms, these are called **Propellanes**.

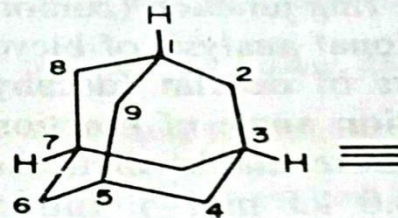
A tricyclic compound may be formed by 4 bridgehead carbon atoms as in case of **Admantane**.(C-3,C-5,C-7,C-10)



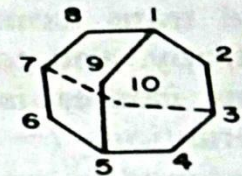
Tricyclo[1.1.1.0]pentane



Tricyclo[3.2.1.0] octane



(LXX)



(LXXa)

We have
awesome
chemistry



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90 Th Thorium 232.03806	7 N Nitrogen 14.0067	19 K Potassium 39.0983
39 Y Yttrium 88.90625	8 O Oxygen 15.9994	92 U Uranium 238.02891