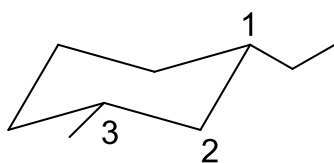
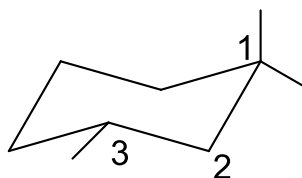

Topics covered in lecture 9-11 to be discussed in Tutorial 5

- Detailed conformational analysis of cyclohexane: Chair & boat conformations, drawing structures, axial, equatorial bonds, stability in mono and disubstituted cyclohexane and various interactions between substituents.
- Isomerism: constitutional, enantiomer, diastereomer, optical activity, specific rotation, %ee, determination of absolute configuration (R/S assignment).
- Fischer projections and its manipulation, R/S assignment in Fischer projections, molecules with multiple stereogenic centers, Relationship b/w various stereoisomers, Meso-compounds, atropisomerism/ conformational isomerism: biphenyls, allenes.

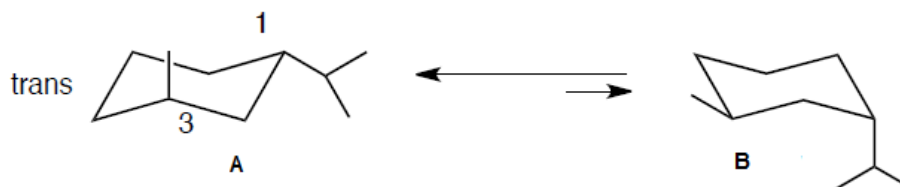
1. Draw the most stable conformations of**(a) cis-1-ethyl-3-methyl cyclohexane.**

Hint: 1,3 Cis- is *e/e* or *a/a*. In eq. form both substituents will avoid 1,3-diaxial interaction.

(b) 1,1,3-trimethyl cyclohexane

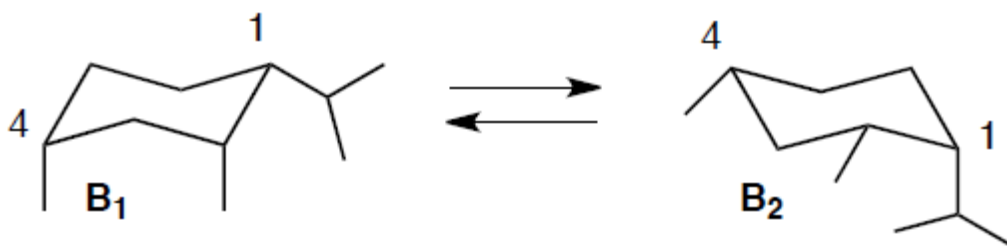
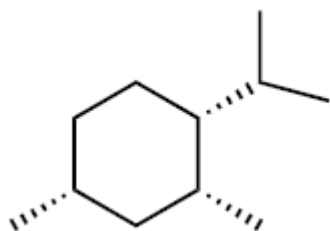
Hint: Me at C3 will be in equatorial to avoid 1,3 diaxial interaction.

Note that it's still have one 1,3-diaxial interaction at C1, though we can not avoid it.

(c) trans-1-isopropyl-3-methylcyclohexane

Two trans- conformation (*e/a*) is possible (**A**, **B**) by placing substituents in *e* or *a* position at C1 & C3. Conformation **A** is lower in energy than conformation **B**, since the larger isopropyl group having stronger 1,3 di-axial interaction is in the less crowded equatorial position in **A**.

2. Draw the both the chair conformation (interconvert by means of the ring-flip) present in equilibrium for following compound. Comment on their relative stabilities.



B₁ and **B₂** are approx.. similar in energy; **B₁** has two axial methyls but **B₂** has the axial isopropyl, the large substituent so they tend to balance the overall energy cost.

3. (i) When 0.300 g of natural cholesterol is dissolved in 15.0 mL of chloroform and placed in a 10.0 cm polarimeter tube, the observed rotation at 20 °C using sodium D-line is – 0.630°. Calculate the specific rotation of cholesterol.

(ii) A mixture of natural cholesterol and its enantiomer has a specific rotation at 20 °C of –27. Calculate %ee (%enantiomeric excess) of this mixture. What % of the mixture is natural cholesterol?

$$(i) [\alpha] = \alpha / c \times l$$

$$[\alpha] = -0.630 / (0.300 \text{ g}/15 \text{ mL}) \times (1.0 \text{ dm})$$

$$[\alpha]_{\text{D}}^{20} = -31.5^{\circ} \text{ (Ans)}$$

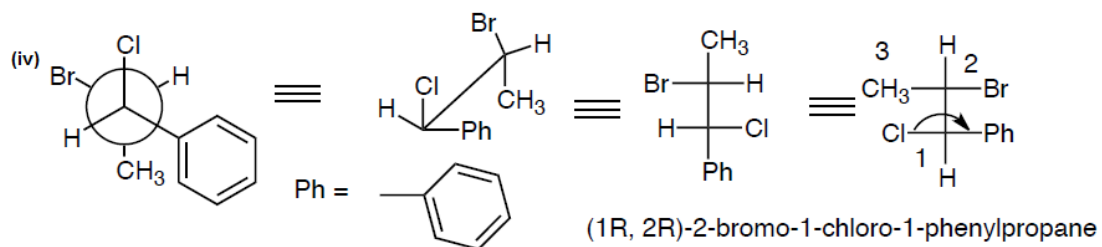
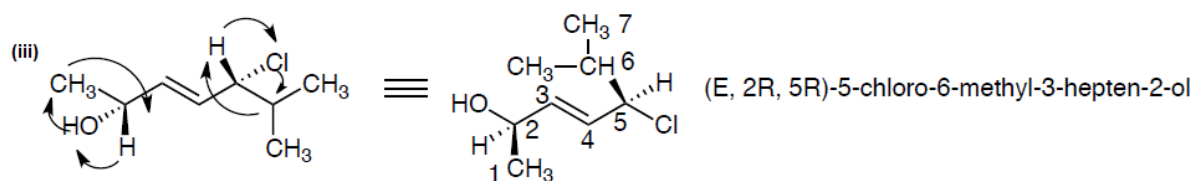
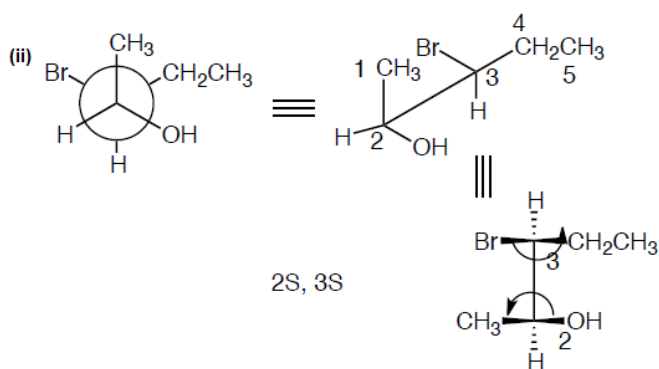
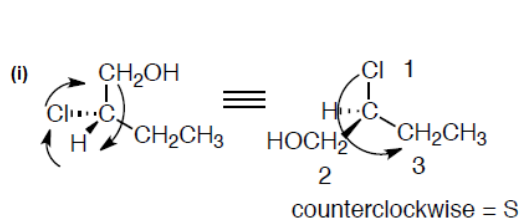
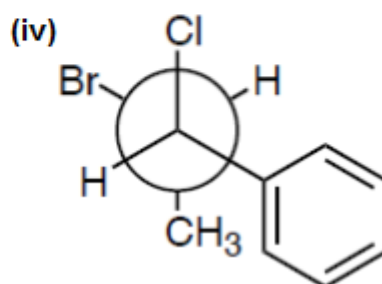
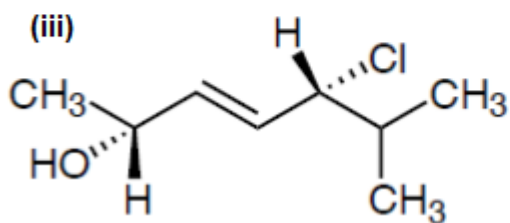
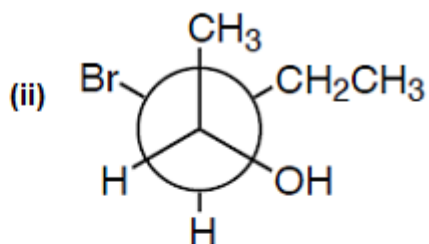
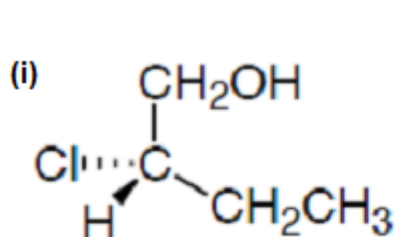
$$(ii) \%ee = \{ \text{observed } [\alpha] / [\alpha] \text{ of pure enantiomer} \} \times 100$$

$$\text{So, } \%ee = (-27 / -31.5) \times 100 = 86\% \text{ (Ans)}$$

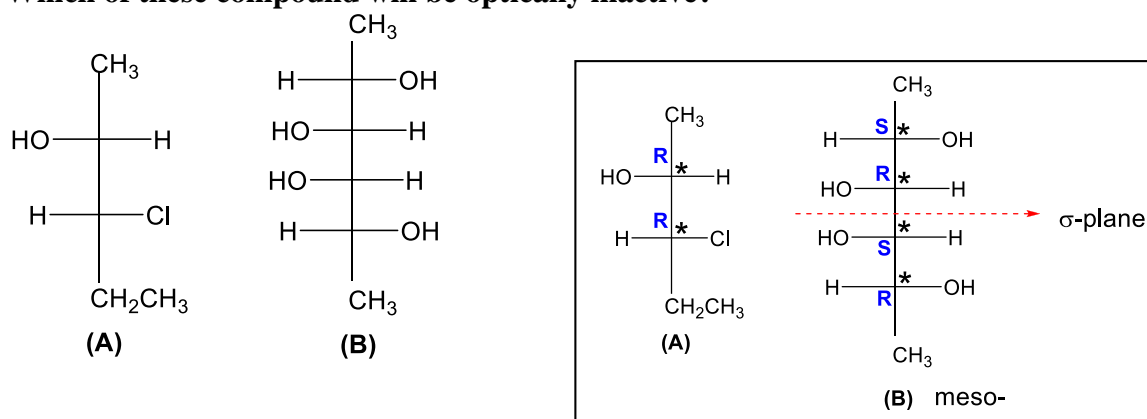
So, % racemic mixture = (100-86) = 14% consists of 7% of natural chl. + 7% enantiomer.

Therefore, Total % of natural cholesterol = (86 + 7)% = **93% (Ans)**

4. Assign the absolute configuration (R or S) to each chirality center.

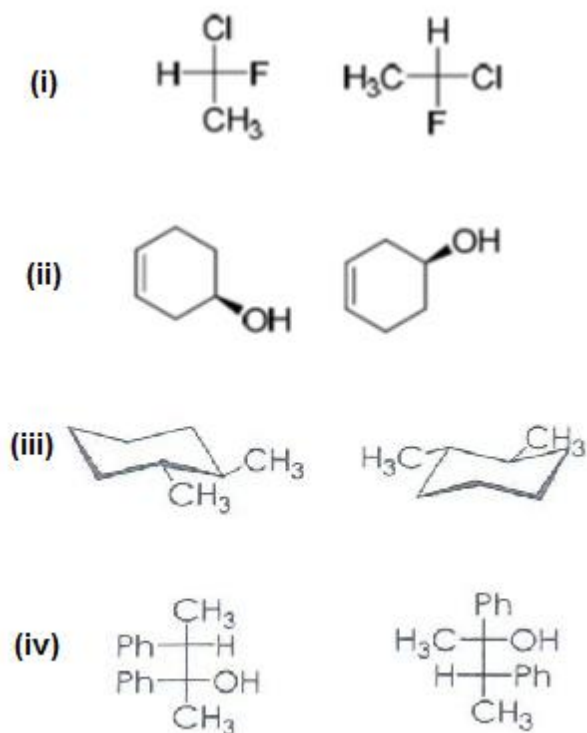


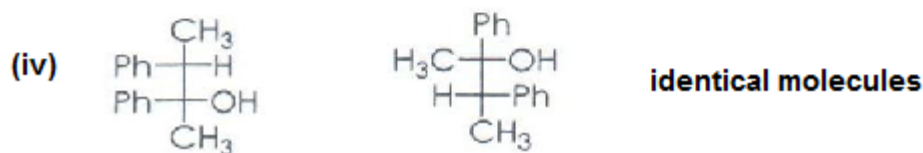
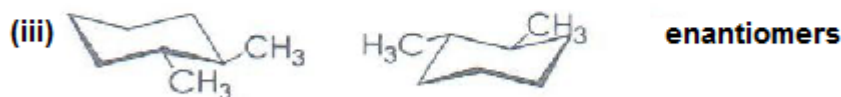
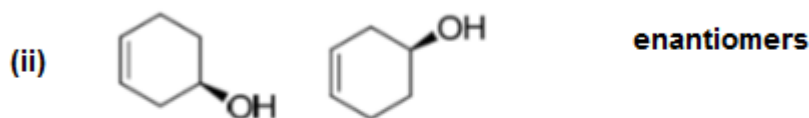
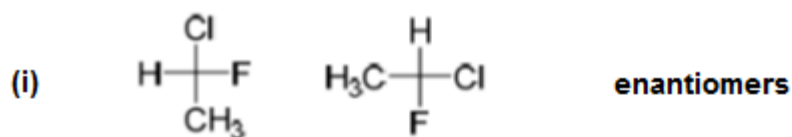
5. Determine absolute configuration of each chirality centers in the following molecules. Which of these compound will be optically inactive?



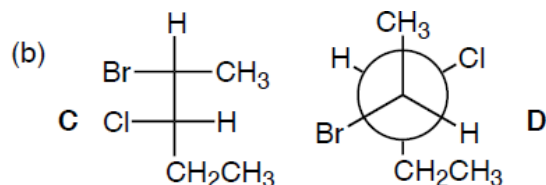
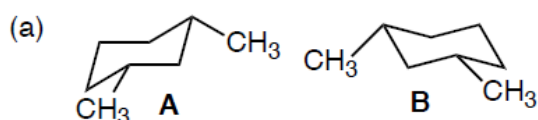
(B) is having mirror plane of symmetry (σ), thus it's achiral and meso compound without any optical activity.

6. Identify the relationship between following molecules as enantiomers, diastereomers, conformers or identical molecules.

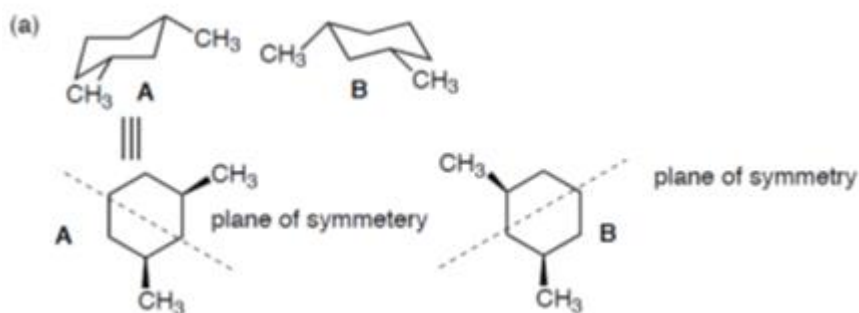




7. Give the relationship between the following molecules. They may be the same molecule, different molecules, constitutional isomers, enantiomers, or diastereomers. Show your work for partial credit.

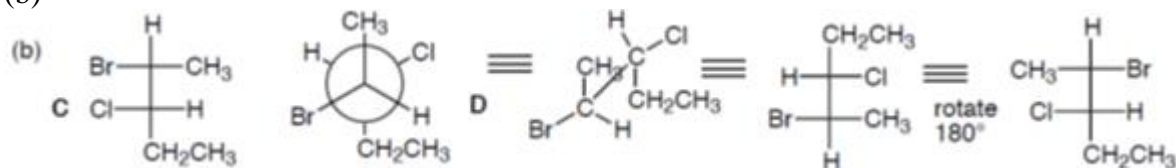


Ans: (a)



Both A and B have a plane of symmetry. They are mirror images but due to presence of plane of symmetry, they are superimposable on their mirror image. So, A & B are the SAME molecule.

(b)



C and D are DIASTEREOMERS; one chirality center is the same, the other is switched; therefore they are not mirror images and they are not superimposable.

8. Draw the possible enantiomers for 2,3-pentadiene.

Answer the following questions:

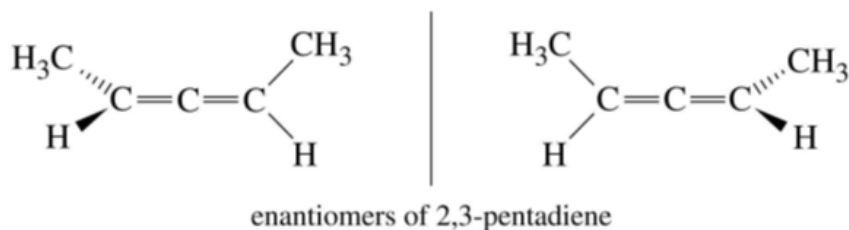
(a) **Point out the type of hybridization of each carbon.**

(b) **Show the overlap of orbitals involved in formation of pi-bonds.**

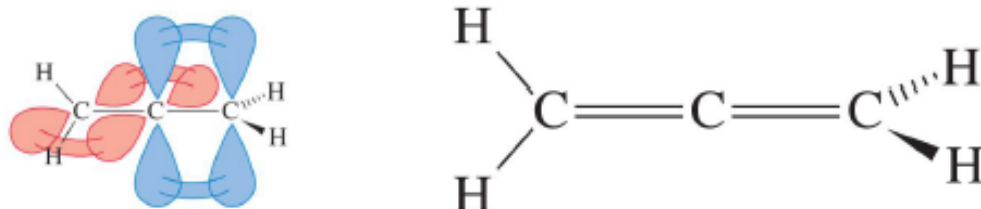
(c) **Is there any chirality center present in this molecule?**

(d) **Will it show any optical activity?**

(a)



(b)

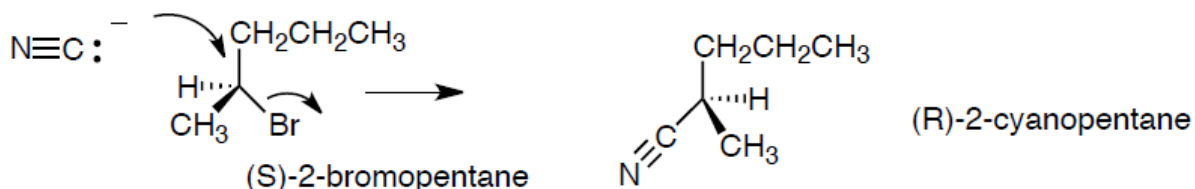


(c) No chirality center present in this molecule. It's having chiral axis.

(d) Yes, it will show optical activity as it's asymmetric molecule.

9. Show the reaction that occurs between (S)-2-bromopentane and cyanide anion (NC⁻).

Assign the absolute configuration to the product. (To be discussed in detail in class 12)



S_N2 mechanism invert the configuration at the carbon atom of the substrate.