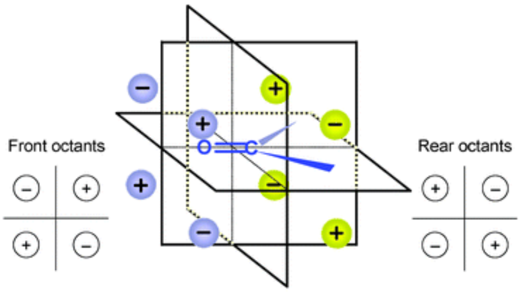
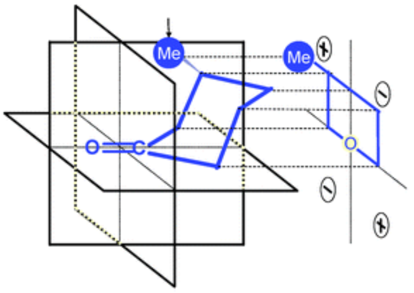
Circular birefringence: When plane polarized light passes through a chiral medium the velocities of right circularly polarized light (r-cpl) and left circularly polarized light (l-cpl) ~~slow~~ are slowed down but to a different extent. That means the velocities of r-cpl & l-cpl are different in chiral medium. This is called circular ~~bir~~ birefringence.

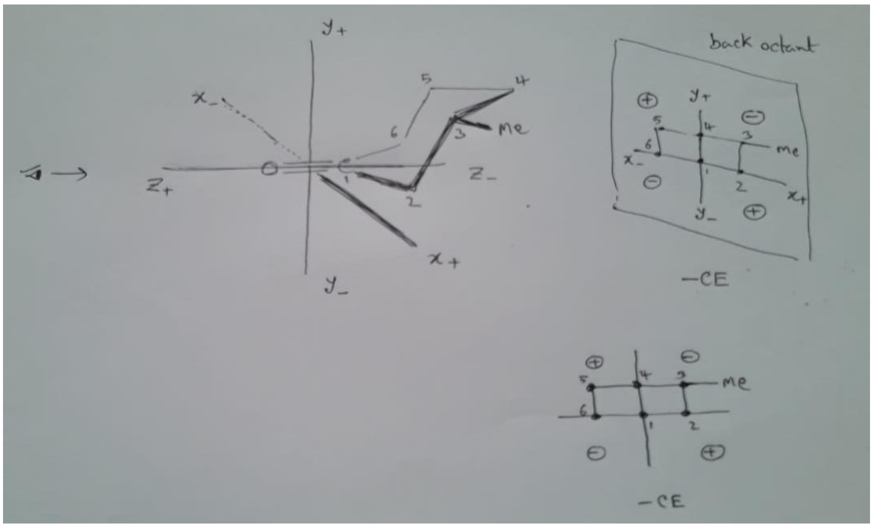
Fresnel equation/ law: As the plane polarized light passes through chiral medium the velocities and hence the refractive index of r-cpl & l-cpl become different. Means $C_R \neq C_L$ and $n_R \neq n_L$. According to Fresnel's law

$$\alpha = \frac{(n_R - n_L)\pi l}{\lambda_0} \quad \text{or} \quad \alpha = \frac{(n_R - n_L)1800 l}{\lambda_0}$$

Here α = observed rotation, n_R, n_L are refractive indexes of R-CPL & L-CPL in chiral medium, l = path length (in cm in 1st eq & in dcm in 2nd eq.) λ_0 = wave length of light in vacuum

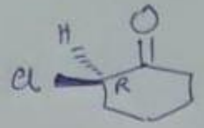


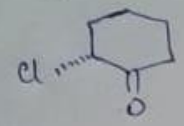


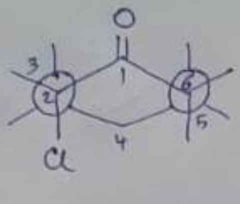


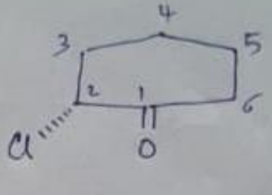
Q3) Predict the sign of Cotton effect with proper octant projection of the following molecules.

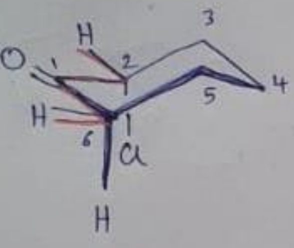
(R)-2-Chlorocyclohexanone

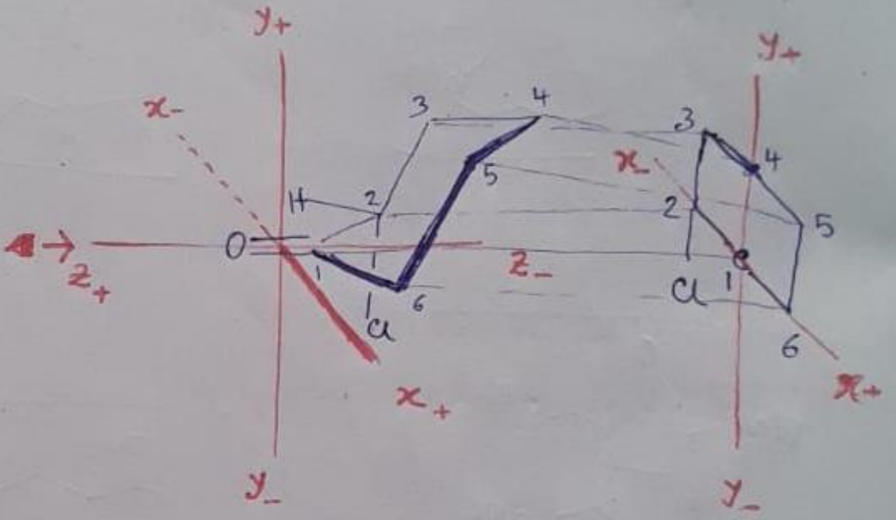


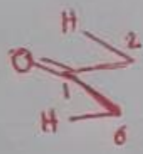




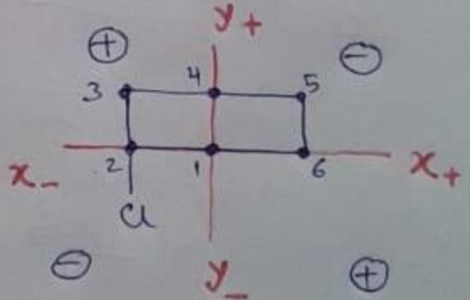








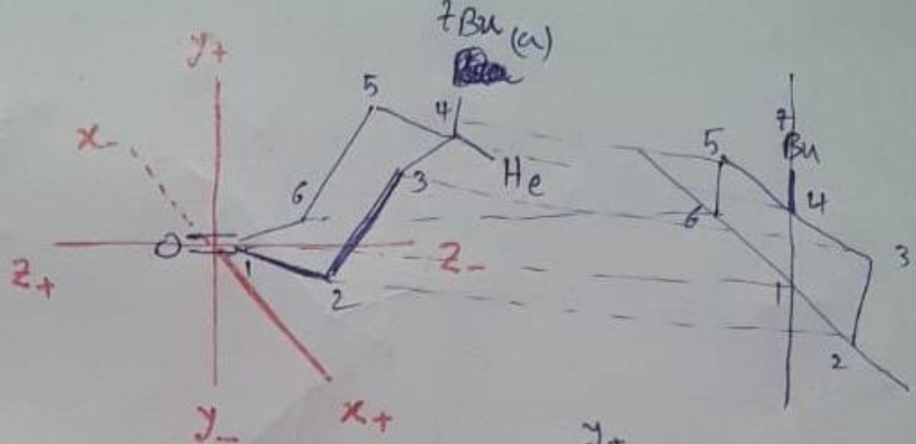
All these atoms $H-C_2-\underset{\overset{\|}{O}}{C_1}-C_6-H$ are on the same plane (xz plane).

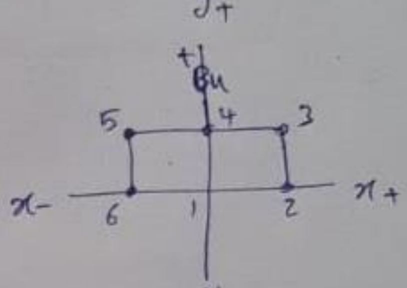


(-CE)

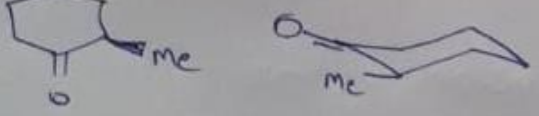
Since -Cl atom falls into rear-lower-left octant, where the sign is negative. So (R)-2-chlorocyclohexanone shows (-ve) cotton effect.

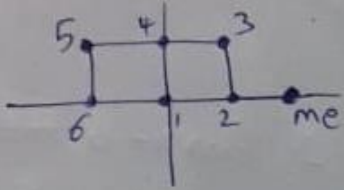
4-^{t}Bu-cyclohexanone , achiral, optically inactive so it will not show any cotton effect





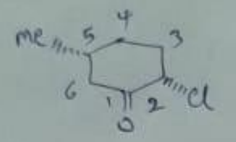
No CE

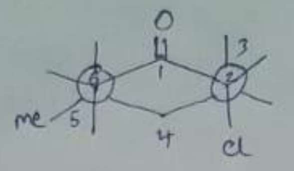


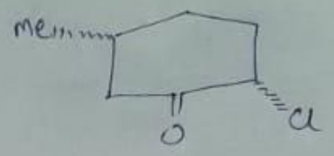


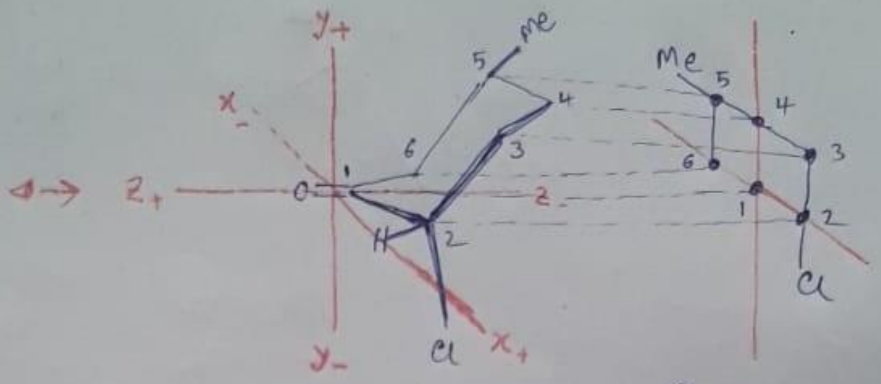
almost zero CE

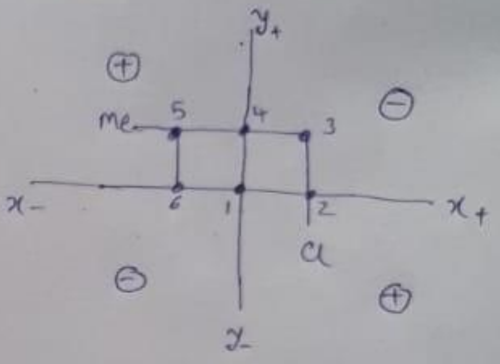
(2S,5R) – 2-Chloro-5-methylcyclohexanone





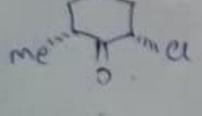


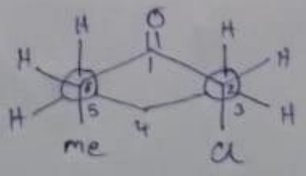


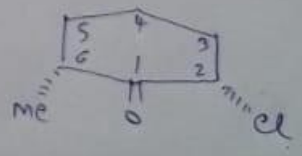


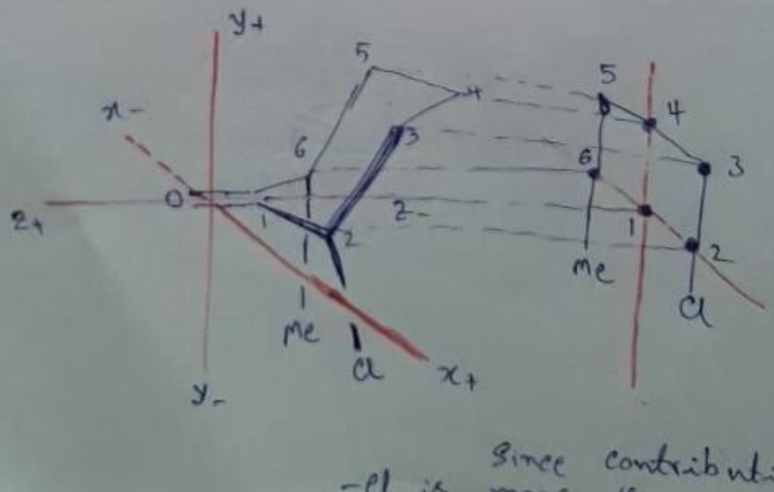
(+CE)

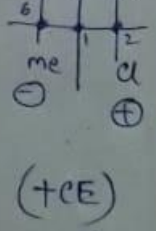
(2S, 6R) – 2-Chloro-6-methylcyclohexanone







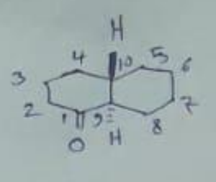


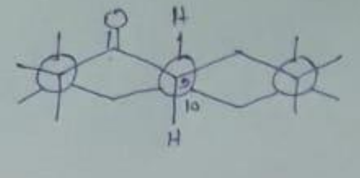


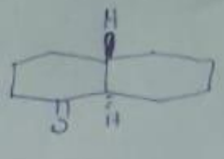
(+CE)

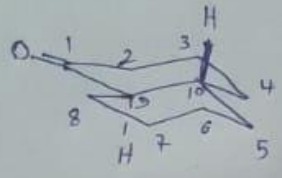
Since contribution of -Cl is more than -Me

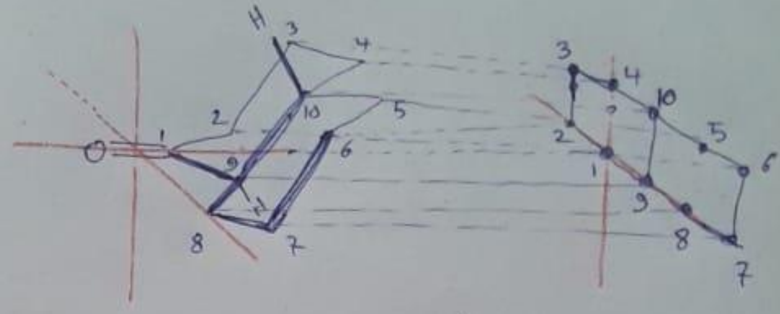
~~(9R,10S)-1-Cyclodecalone~~ (9R,10S) - 1- Decalone

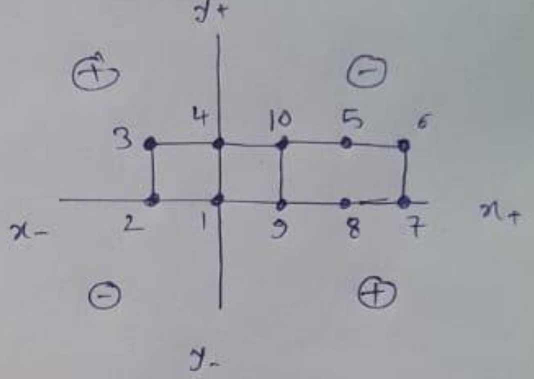






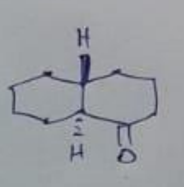


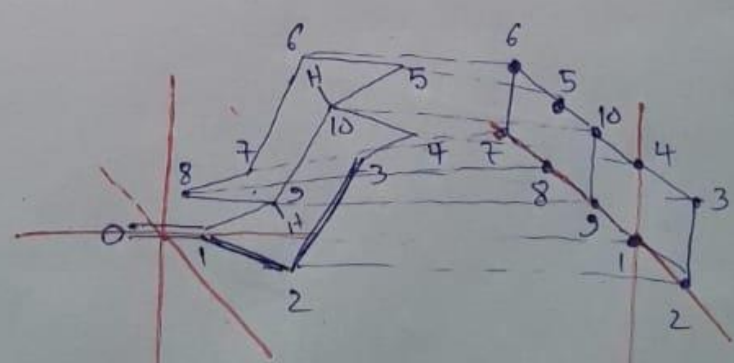


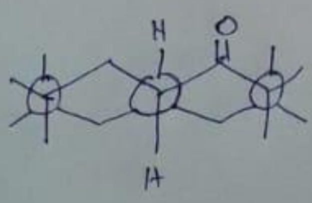


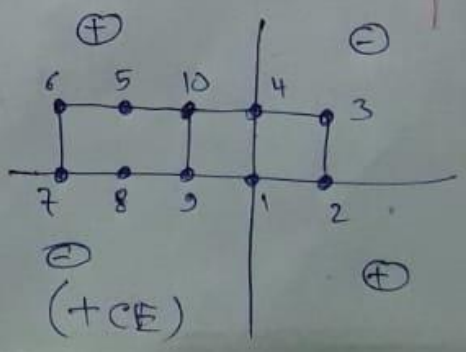
(−CE)

(9S,10R) - 1 - Decalone

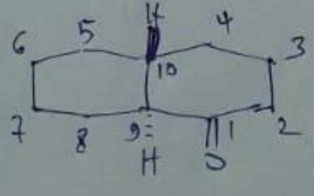








(+CE)



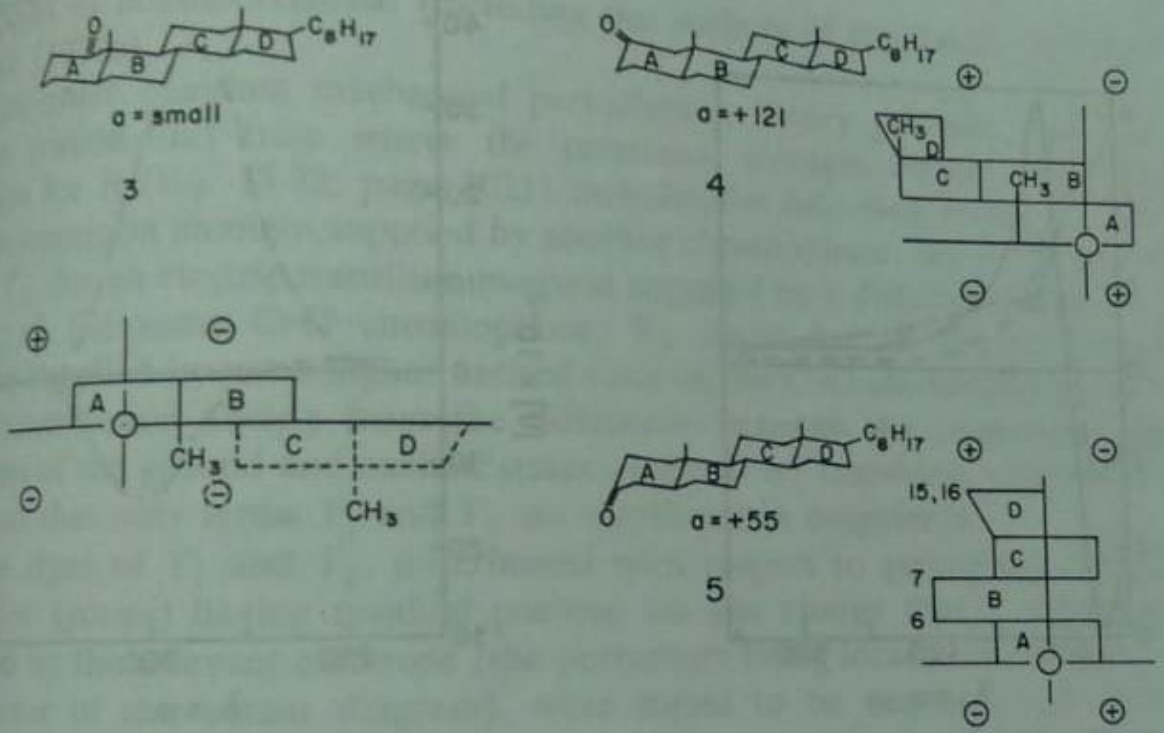
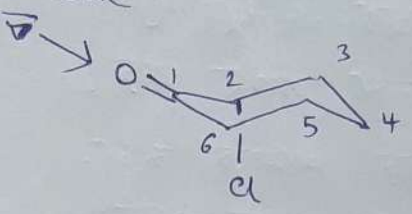


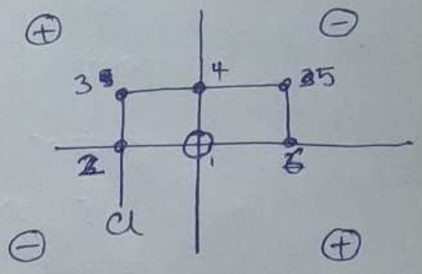
figure 13.32. Semiquantitative assessment of CE magnitudes. Octant rule projection for isomeric 1-, 2-, and 3-cholestanones (**3–5**, respectively) and experimentally observed CE amplitudes (see Figs. 13.33 and 13.34, respectively). The projection outlined with dashed lines is that in a front octant. [Adapted with permission from Snatzke, G., *Angew. Chem. Int. Ed. Engl.*, **7**, 14 (1968).]

tive assessment of CE magnitudes is often possible: The larger the number of carbon atoms, groups, and/or rings in a given sector, uncompensated by like contributi of opposite sign, the greater the CE magnitude. The

~~Sigh~~ Sign of CE with octant projection diagram

(R)-2-Chlorocyclohexanone

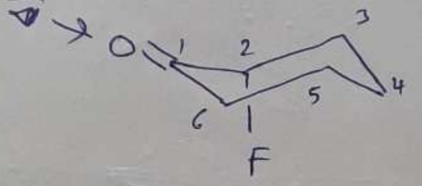


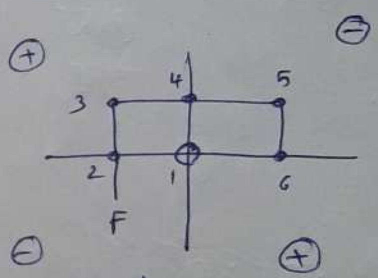


(−ve) CE

As chlorine atom falls on rear lower left ~~quadrant~~ octant, so the sign of CE is ~~no~~ negative.

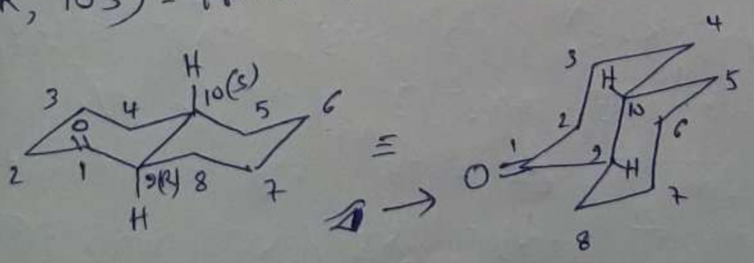
(R)- 2- Fluorocyclohexane

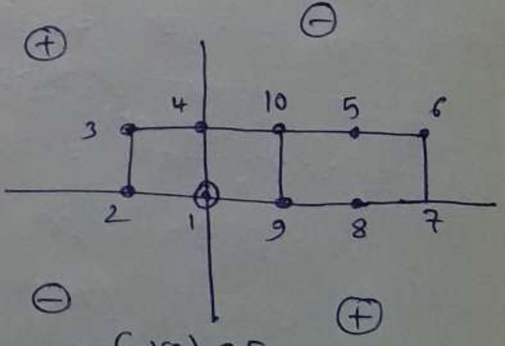




As F falls on rear lower left ~~quadrant~~ octant and F atom is highly electronegative, so it shows (+ve) CE.

(9R, 10S) - trans - 1- decalone





(−ve) CE

As majority of C & H atoms fall in rear upper right ~~quadrant (or octant)~~ octant, so the sign of CE is negative.

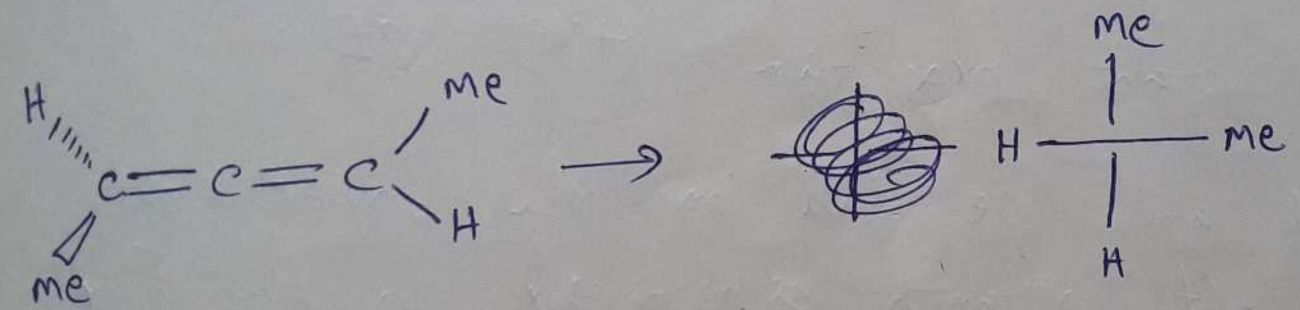
1) Explain the characteristic features of CD & ORD. Predict the sign of

---

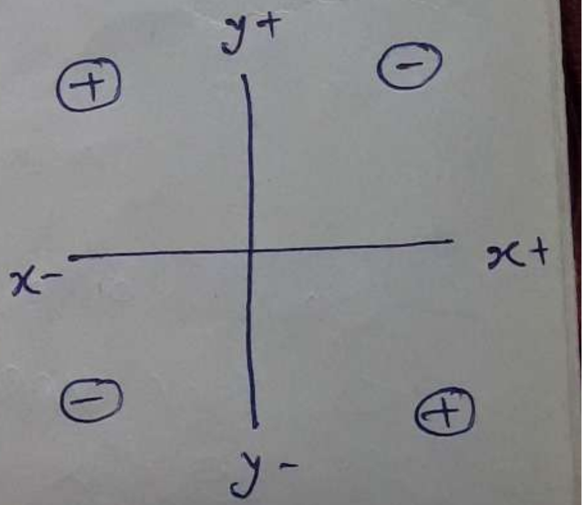
Sign of Cotton effect with octant projection

~~2C-Elea~~ i) (Ra)-1,3-Dimethyl allene

1→



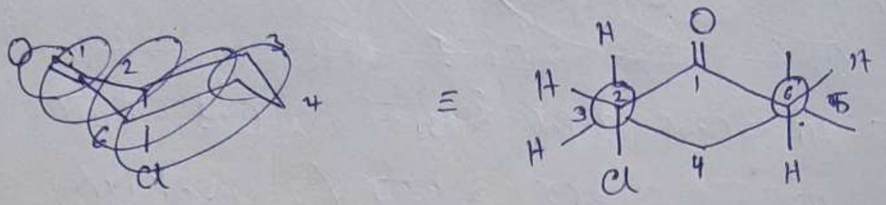
(Ra)



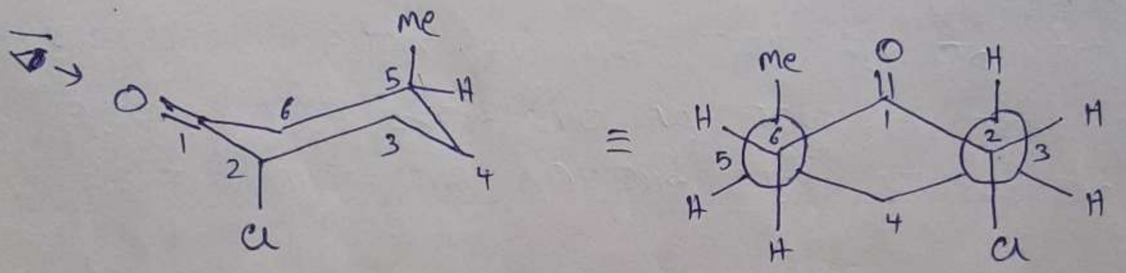
Octant projection

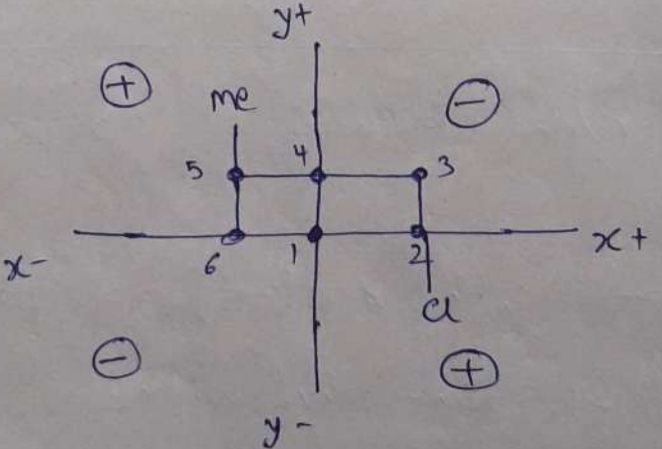
Sign of CE with octant projection

i) (2S, 5R) - 2-Chloro- 5-methylcyclohexanone



Sign of CE with octant projection

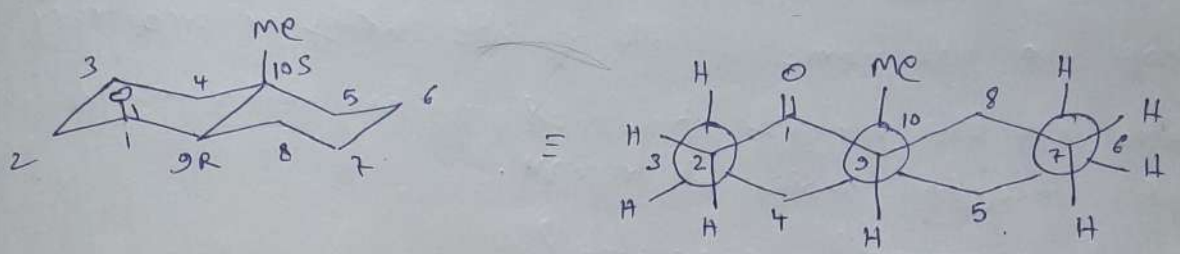


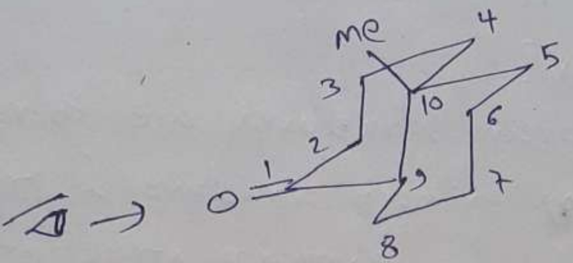


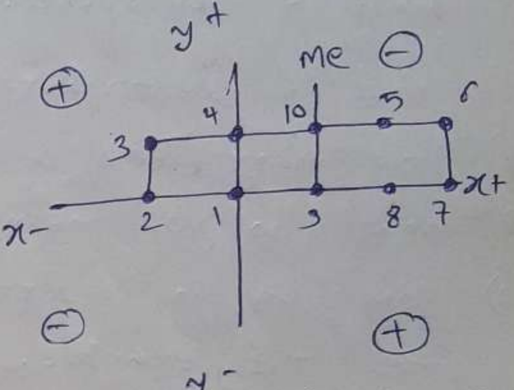
octant projection (+ve) CE

Since both -Cl and -me fall on rear lower right & rear upper left octants respectively. So the sign of CE is (+ve).

(ii) (9R, 10S)- trans-10-Methyl-1-decalone



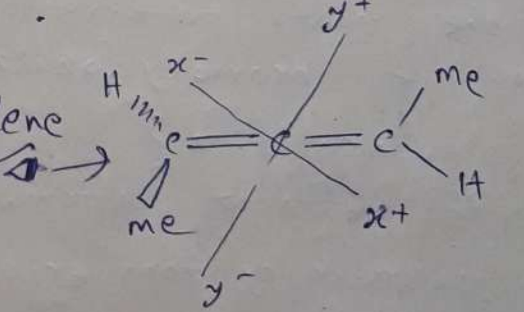


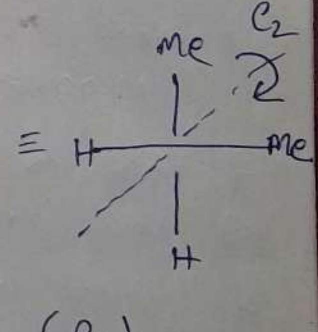


(−ve) CE
Octant projection

As most of the C & H atoms fall in rear upper right octant, so the CE is (−ve).

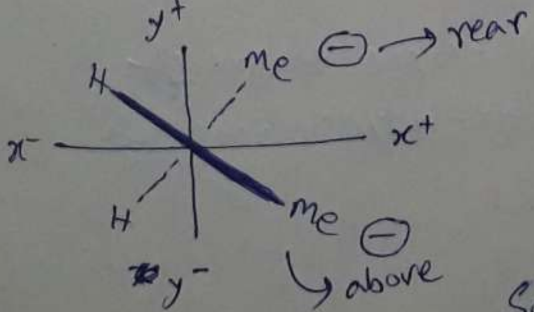
(iii) (Ra) - 1,3-Dimethyl allene





(Ra)

We have to place the origin (0,0,0) of x, y, z 3D axis at the central 'C' atom along C_2 axis of allene. So one −Me gr. will fall in rear upper right octant and another −Me gr will fall in above lower right octant So the sign of CE is negative (−ve)

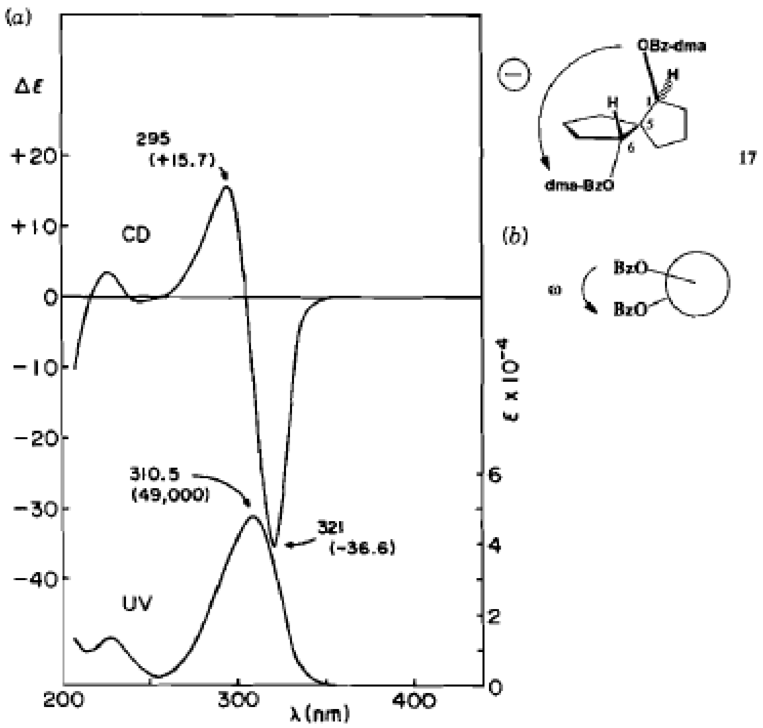


negative (−ve) CE

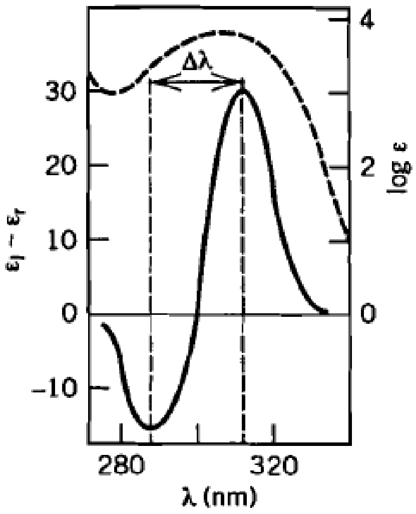
What is exciton chirality? Explain with diagram, what is Davydov splitting.

When two chromophores are in close spatial proximity to one another and so disposed that a chiral array results, interaction (dynamic coupling) between the individual chromophores gives rise to characteristic CE couplets, in the CD spectrum. This is known as exciton coupling or exciton chirality. From this the configuration of the chiral array may be easily deduced.

For example, this method is used for determining the configuration of glycols from the sign of the CE of the strong p-p* transition of the glycol dibenzoate derivatives (You can give the graph and Δε vs λ scale values only approximately, no need to give the inside values)

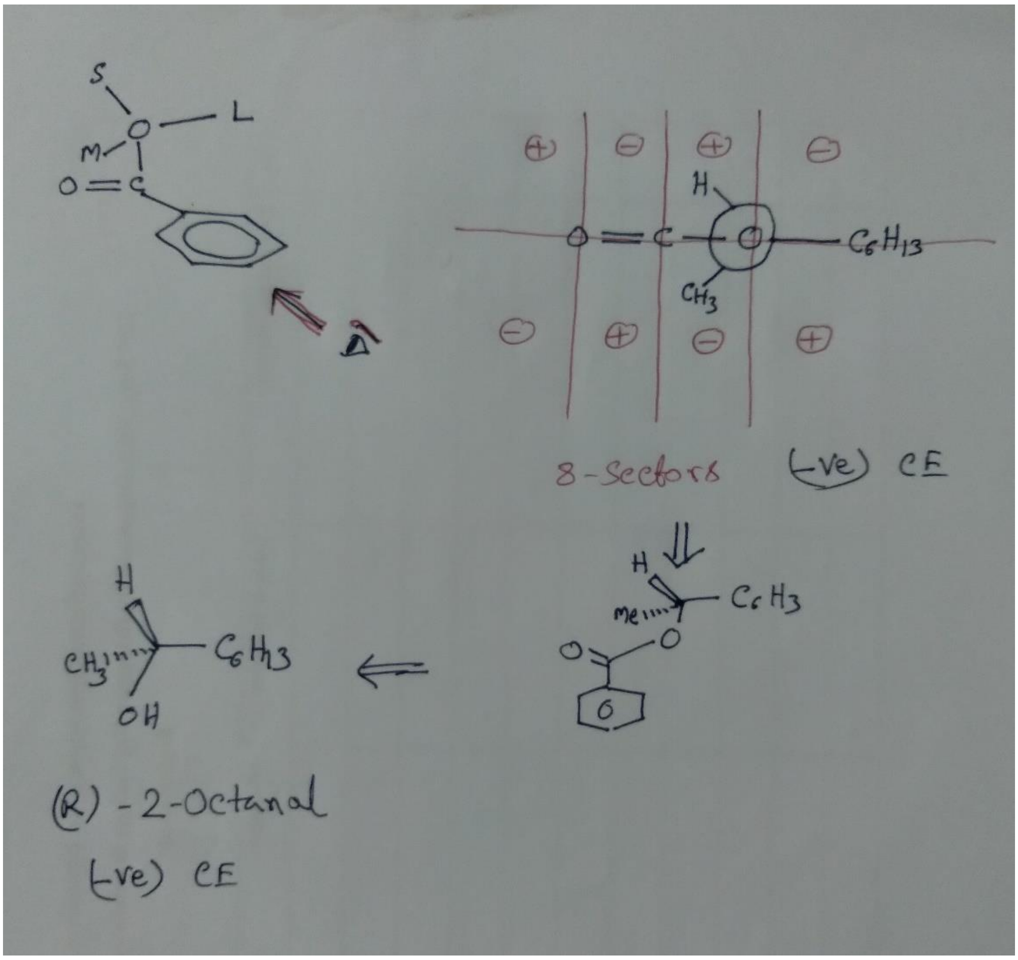


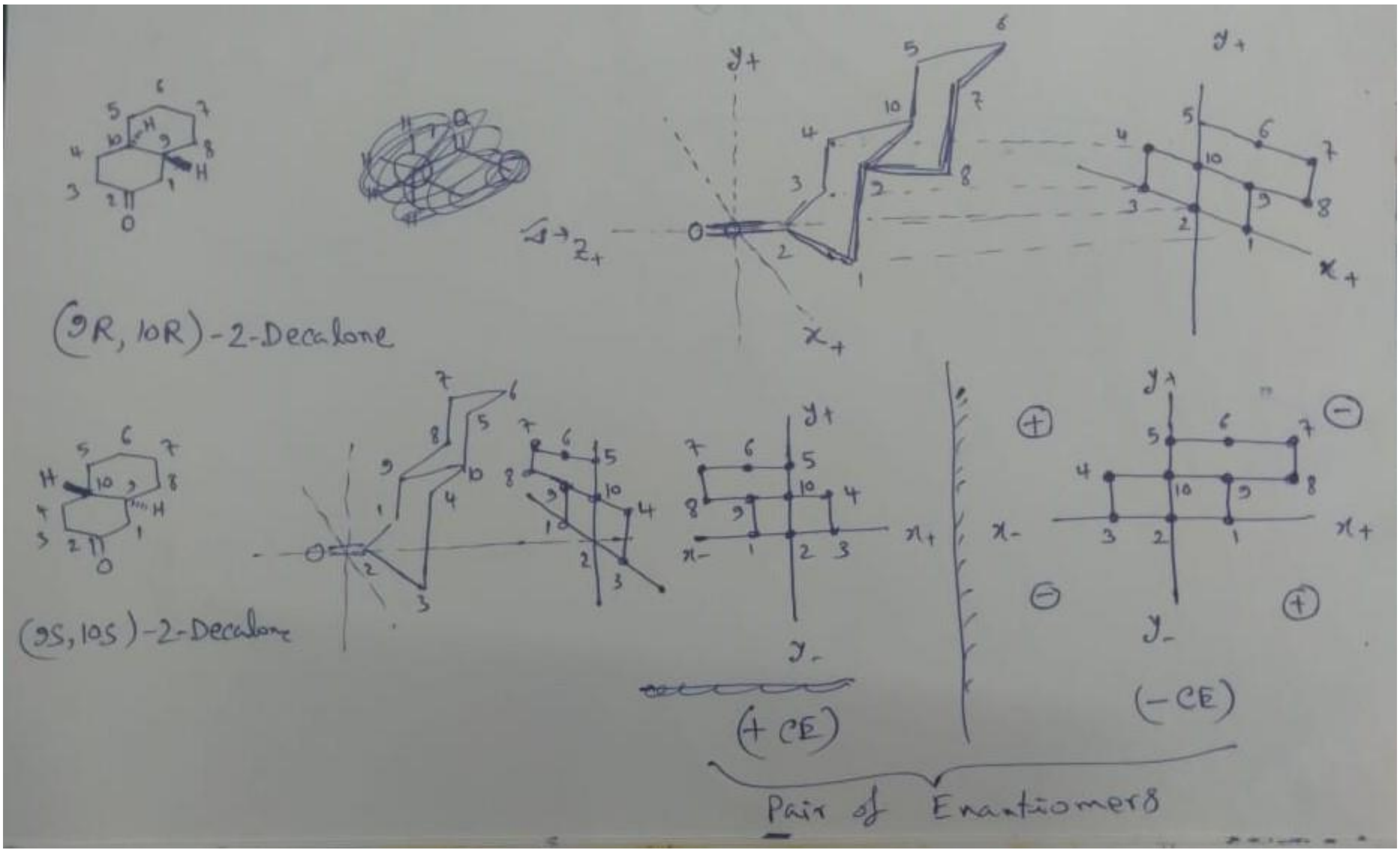
In this exciton coupled spectra the difference between the wavelength of minima and maxima is known as Davydov splitting as shown below.



The benzoate ester of a given 2-octanol shows negative Cotton effect (-) CE. Applying the benzoate sector rule, find out its absolute configuration.

The benzoate ester is prepared with the given 2-octanol and the Cotton effect is determined. It is given that the CE is negative. According to benzoate sector rule we have to look the molecule from the plane of benzene ring. Now it is divided into 8 sectors (as shown below). Then the large group is placed anti periplanar with respect to C=O. If the medium group goes to negative sector, then it will show negative CE. So, following this rule if we do a retro analysis, we can find that when the CE is negative the absolute configuration of the 2-octanol is (R).





Relation between molar ellipticity [θ] of CD curve and intensity (Δε) of CD curve.

$$[\theta] = 3298.2\,\Delta\varepsilon$$

Relation between molar ellipticity [θ] of CD curve and molar amplitude (a) of ORD curve.

$$a = 0.0122\,[\theta]$$

Relation between intensity (Δε) of CD curve and molar amplitude (a) of ORD curve.

$$a = 40.28\,\Delta\varepsilon$$

The observed optical rotation α is proportional to the concentration of the optically active molecules and path length of the solution through which polarised light has traversed. This is known as Biot's law.

$\alpha = [\alpha].\ c.\ l$ [where c = concentration of the compound in gm per ml, l = length of the tube in dm], where $[\alpha]$ = proportionality constant and is called *specific rotation.*

- ***Specific rotation*:**

The *specific rotation,* $[\alpha]$, may be defined as the rotation in degrees brought about by a pure transparent liquid or a solution containing 1g of an optically active substance per ml of solution, placed in a 1 decimetre polarimeter tube.

Specific rotation is related to observed rotation by the following equation.

$$[\alpha]_{\lambda}^{t^{\circ}C} = \frac{100 \times \alpha}{l \times c} \text{ --------------------- equation 3.1}$$

where, λ=wave length of polarised light (generally yellow line of sodium vapour light (λ= 5893 nm is used)

$t^{\circ}C$ = experimental temperature,
α = observed angle of rotation in degrees
l = length of solution in dm ≡ length of the polarimeter tube in dm
c = concentration of the solution g /100 mL

When pure transparent liquid (neat liquid) is taken, the expression used is,

$$[\alpha]_{\lambda}^{t^{\circ}C} = \frac{\alpha}{l \times d} \text{ ----- eq. 3.2}$$

activity is not a collegative property.

Since optical property of stereoisomers is associated with chirality, measurement of optical property is called *Chiroptical method*. Other *Chiroptical methods* are ORD (optical rotations dispersion) and CD (circular dichronism). These are discussed in short latter in this Chapter.

- ***Molecular rotation or Molar rotation*:**

$$[\Phi]_{\lambda}^{t^{\circ}C} = \frac{[\alpha] \times M}{100} \text{ ----------------- equation 3.3}$$

Where, $[\Phi]$ = molar rotation
$[\alpha]$ = specific rotation
M = molar mass of the substance

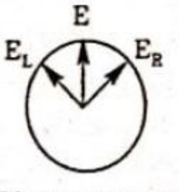
For a substance of molecular weight 100, molar and specific rotation are the same.

3.3. Circular Dicroism:

When an optically active compound is also capable of absorbing light, then an unequal absoption of the two components vectors (circularly polarised components) is usually found. The phenomenon of the differential absoption of the right and left circularly polarised light is called *circular dicroism*, usually abbreviated to CD.

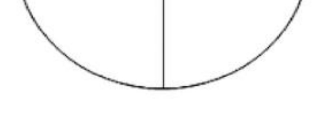
An electronic or vibrational transition of energy states associated with a chiroptic chromophore in a chiral molecule causes right and left circularly polarised to be absorbed differentially. If A_L and A_D represents absoptions of left and right circularly polarised light, then in case of CD, anisotropic absoption takes place, i.e., $A_L \neq A_D$ and $\Delta A = (A_L - A_D)$ and is a measure of the CD. If the molar concentrations are known then according to Lambert and Beer's law, $\Delta A = \Delta A \approx \varepsilon\ c\ l$, where c is the concentrationin moles per litre and l is the path length in centimetres (cm). We may write $\varepsilon_L - \varepsilon_R = \Delta\varepsilon$, where ε_L and ε_R are molar absoption coefficient for left and right circularly polarised light, respectively, at the absobption wavelength.

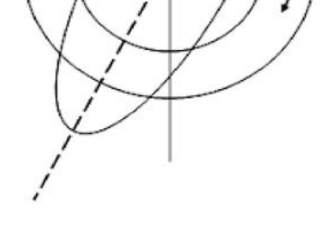
Since in case of CD, $A_L \neq A_D$ and from Lambert-Beer's law, we get $A = \log (I_o/I)$, where I_o is the intensity of the impinging light while I is that of the transmitted light, the two circularly polarised components are now of unequal intensity ($I_L \neq I_R$). During the passage of light through the sample in a region where absorption takes place, the incident linearly polarised light is converted into elliptically polarised light, that is, the resultant electric field vector traces an elliptical path. In general the major axis of this ellipse is much greater than the minor axis, and for the purpose of measurment may be treated as plane polarised light. The eccentricity of the ellipse $[(a-b)/a]$ is 1 for linearly polarised light ($b=0$), and 0 (zero) for circularly polarised light ($a=b$). The major axis of the ellipse traces the angle α and the ellipticity ψ is defined by the expression, $\tan \psi = b/a$, where b=minor axis and a=major axis of the elliptical vector respectively, of the ellipse that characterises the elliptically polarised light.



Plane polarized light

Elliptically polarised light produced from
Plane polarised light by differential absorption





Like rotation α , it is possible to define a specific ellipticity $[\psi]$ and a molar ellipticity $[\theta]$ as shown below, where the symbols c, l, and M as they do in the definitions of specific rotation and molar rotation.

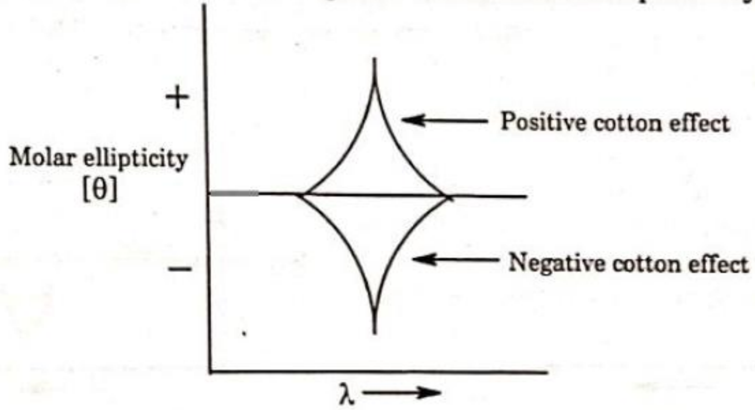
$$[\psi] = \frac{\psi}{c\,l} \text{ in } 10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$$

$$[\theta] = \frac{[\psi]M}{100} \text{ in } 10 \text{ deg cm}^2 \text{ mol}^{-1}$$

When the ellepticity is small, which is a common occurance, $\tan\psi \cong \psi$, and latter is proportionalto ΔA. Under this conditions, the circular dichroism is quantitatively expressed as

$$[\theta] = 3298.2\Delta\varepsilon$$

When this differential absorption or molar ellipticity is plotted against wavelength of the polarised light, a curve closely related to the electronic absorption spectrum (UV spectrum) is obtained. These are called CD curves. This curve can be either positive or negative (Fig. 37) and termed as positive Cotton effect and negative Cotton effect respectively.



CD curves

Fig. 3.7

CD bands are narrow and usually non-overlapping even in the presence of more than one absorbing chromophore. Again, the amplitude of the CD cotton effect is related to molecular dissymmetry. The sign and amplitude of the Cotton effecting CD curves may be used to determine conformation of a molecule provided the absolute configuration is known. Enantiomers have opposite sign of Cotton effect; however the magnitude of amplitude is same.

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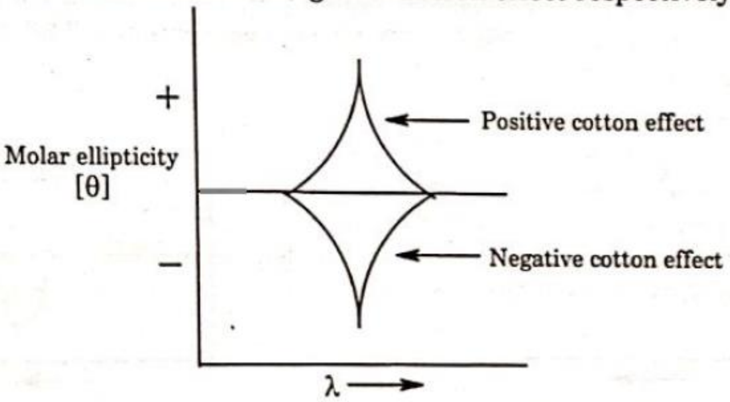

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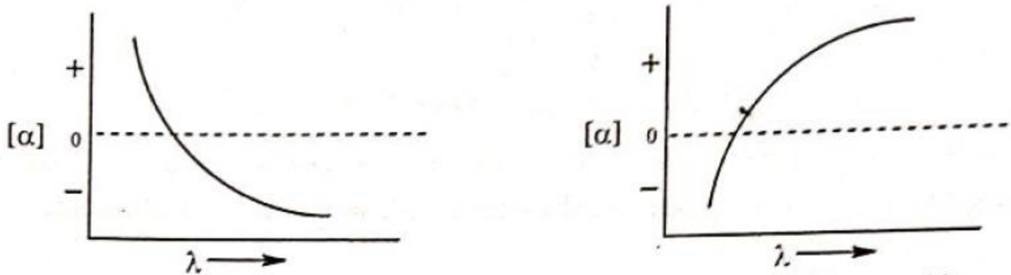
3.4. Optical Ratatory Dispersion:

Optical rotatory dispersion method consists in the plotting of variation of optical rotation $[\alpha]$ as a function of wavelength (λ) in the polarised light, usually abbreviated as ORD. Refrative index for right and left circularly polarised light varies strongly with wavelength, particularly in the region of a chromophore (a molecular feature that has an electronic transition in the observed region, e.g. C=O, C_6H_5, conjugated alkenes). Two types of chromophore are observed. An inherently *dissymmetric chromophore* is one that is chiral and lies on an axix or in a plane of chirality. An asymmetrically or disymmetrically perturbed chromophore, which is itself achiral but is influenced by neighbouring chirality.

The variation of specific rotation, $[\alpha]$ with $[\lambda]$ can belong to one of the above two types. In the absence of any chromophore, as mentioned above, a simple ORD curve is observed (Fig.3.8).

An enantiomer that gives a steady increase in rotation, not necessarily involving a change of sign, from high to low wavelengths is said to exhibit a positive cotton effect and opposite is a negative cotton effect.

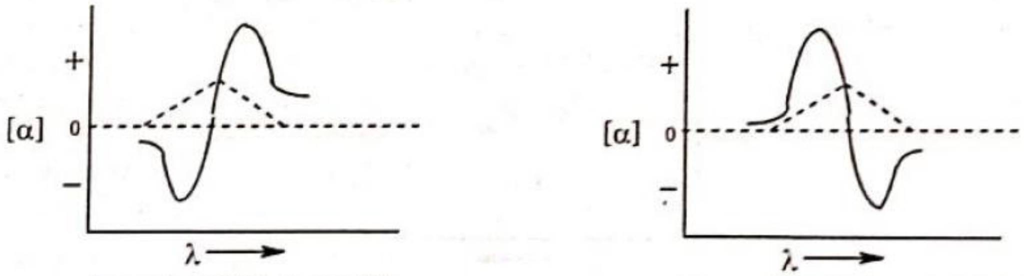


Simple ORD curve with positive Cotton effect

Simple ORD curve with negative Cotton effect

Fig. 3.8

When a chromophore of either type is present, then anomalous Cotton effect is observed, as shown in the Fig. 3.9. A molecule is said to exhibit positive cotton effect if the curve shows a peak before a trough when going from high to low wavelength. The opposite is called a negative Cotton effect.



Anomalous ORD curves with negative Cotton effect
Dotted curve represents the absorption spectrum

Anomalous ORD curves with positive Cotton effect
Dotted curve represents the absorption spectrum

Fig. 3.9

The amplitude of the Cotton effect is the difference in specific rotation between the highest maximum and the lowest minimum. The amplitude of ORD curve is useful guide to the presence of inherently dissymmetric chromophores. The amplitude of the Cotton effect is a measure of the power of the optical rotation and can be correlated with molecular dissymmetry. Like CD, the sign and amplitude of the Cotton effect in ORD curves may be used to determine conformation if the absolute configuration is known. The instrument used for the mesurement of CE in CD and ORD is known as *Spectropolarimeter*.

3.5. Application of ORD and CD in stereochemistry:

The principal application of CD and ORD is in the assingnment of configuration or conformation of molecules. A good application of ORD is determination of configuration of 5-, 6-, and 7-membered cyclic ketones. For this purpose an empirical rule known as *octant rule* has been developed. Cyclohexanones, which exhibit a low intensity λ_{max} (n-π^*) at 290-300 nm, have perhaps been the most widely studied and led to the formulation of the so called octant rule which allows the sign and amplitude of the Cotton effect to be predicted.