

⇒ Numericals

Q Solution of thickness 1 cm, molar absorptivity = 40.9 at 290 nm. If the absorbance is 0.111. Calculate concentration.

Solⁿ.

Lambert's law: $A = \epsilon CL$

ϵ → Molar Absorptivity
 C → concentration
 L → pathlength

pathlength $L = 1 \text{ cm}$

Epsilon $\epsilon = 40.9$

$$A = \epsilon CL \quad \therefore 0.111 = 40.9 \times C \times 1$$

$$\therefore C = 2.71 \times 10^{-3}$$

Q 0.25 M solⁿ, pathlength = 1 cm, absorbance = 0.075 at 560 nm. Calculate

- 1) Molar Absorptivity of solⁿ
- 2) Absorbance if the concⁿ is 0.65 M
- 3) Concentration if absorbance is 0.450.

Solⁿ

1) $A = \epsilon CL$

$$0.075 = \epsilon \times 0.25 \times 1$$

$$\therefore \epsilon = 0.3 \text{ M}^{-1} \text{ cm}^{-1}$$

↳ It is same for solⁿ

2) $A = \epsilon CL$

$$= 0.3 \times 0.65 \times 1$$

$$= \cancel{1.95} \quad 0.195$$

3) $A = \epsilon CL$

$$\cancel{A} \quad 0.45 = 0.3 \times C \times 1$$

$$\therefore C = 1.5 \text{ M}$$

Q Intensity of incident light on a sample is 0.5 W/m^2 & the intensity of light entering the detector is 0.36 W/m^2 . Calculate the transmittance & absorbance.

Ans

$$A = -\log \frac{I_0}{I} = \log \frac{1}{T} = -\log T, \quad T = \frac{0.36}{0.5}$$

$$= -\log \frac{0.5}{0.36}$$

$$= \boxed{0.72}$$

$$= \boxed{+0.143}$$

Q A solⁿ of thickness 3 cm transmits 30% incident light. Calculate the concⁿ given that molar Absorptivity is $4000 \text{ dm}^3 \text{ M}^{-1} \text{ cm}^{-1}$.

Solⁿ

$$A = \epsilon CL$$

$$L = 3 \text{ cm} \quad \epsilon = 4000$$

$$C = ?$$

~~A~~

$$A = -\log T$$

$$= 0.523$$

$$\therefore C = \frac{0.523}{4000 \times 3} = 4.35 \times 10^{-5} \text{ mol/dm}^3$$

Q % T of a solⁿ of unknown compound is 20% at 25°C & 300 nm for a $4 \times 10^{-5} \text{ M}$ solⁿ in 2 cm cell. Calculate

1) A

2) Molar Absorptivity

3) % T of $2 \times 10^{-5} \text{ M}$ solⁿ in 4 cm cell.

Solⁿ

~~A = \epsilon c l~~

1) $A = -\log T = -\log 0.2 = 0.698$

2) $A = \epsilon c l$

$0.698 = \epsilon \times 4 \times 10^{-5} \times 2$

$\therefore \epsilon = \frac{0.698}{8} \times 10^5$

$= \cancel{8625} \quad 8.7 \times 10^3 = 8737.5 \text{ M}^{-1} \text{cm}^{-1}$

3) $A = \epsilon c l$

$A = \cancel{88} 8737.5 \times 2 \times 10^{-5} \times 4$

$\therefore A = -\log T = 0.696$

$T = 10^{-0.696}$

$= 0.2013$

Q

Thickness 2 cm

Transmitted light is 0.12 times of incident light,
Molar Absorptivity is $0.35 \text{ M}^{-1} \text{cm}^{-1}$. Calculate the
concⁿ & absorbance

Solⁿ

$A = \epsilon c l$

~~$-\log T =$~~

Absorbance $= -\log T = -\log 0.12$
 $= 0.92$

$C = \frac{A}{\epsilon l} = \frac{0.92}{0.35 \times 2} = 1.3 \text{ M}$

Q

A solⁿ of thickness 4 cm, transmits 40%.
Calculate concⁿ of solⁿ whose molar
absorptivity is $4000 \text{ dm}^3 \text{ mol}^{-1} \text{cm}^{-1}$ at 280 nm.

Soln

$$A = \epsilon CL$$

$$C = \frac{A}{\epsilon L} = \frac{-\log 0.4}{4000 \times 4} = 2.49 \times 10^{-5} \text{ mol/dm}^3$$

⇒ U-V Spectrophotometer. (spectrometer)

→ To measure the spectrum of compound.

→ In reference cuvette absorbance is 0.
↳ device

→ In TGA we maintain inert ~~temp~~ ^{atmosphere} by generally passing Nitrogen

Q A local radio station transmits at app 95 MHz on its very high ~~A~~. Calculate wavelength

Solⁿ
$$\lambda = \frac{c}{f} = \frac{300}{95} \approx 3.158 \text{ m}$$

IF $f = 810 \text{ kHz}$, $\lambda = 370.37 \text{ m}$

Q IF wave number = 2200 cm^{-1} . Calculate wavelength & freq.

Solⁿ
$$\lambda = 0.045 \text{ m}$$

$$f = 6.6 \times 10^9 \text{ Hz}$$

⇒ Hooke's law.
$$f = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}, \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

IF bond strength = x for C-C
 $= 2x$ " C=C
 $= 3x$ " C≡C

Q Calculate C-H bond freq.

$k = 5 \times 10^5 \text{ gm/sec}^2$

mass of carbon = $20 \times 10^{-24} \text{ g}$

hydrogen = $1.6 \times 10^{-24} \text{ g}$

Solⁿ
$$f = \frac{1}{2\pi} \sqrt{\frac{5 \times 10^5}{\frac{3.2 \times 10^{-47}}{21.6 \times 10^{-24}}}}$$

$$= 9.24 \times 10^{13} \text{ Hz}$$

$$\lambda = \frac{c}{f} = 3.1$$

$$\text{wave number} = \frac{f}{c} = 3.1 \times 10^5 \text{ m}^{-1}$$

Q Calculate the wave numbers of stretching vibration for $C=C$.

Solⁿ

$$f = \frac{1}{2\pi} \sqrt{\frac{2 \times 5 \times 10^5}{\frac{12 \times 12}{24 \times 6.03 \times 10^{23}}}}$$

For double bond

$$= \frac{1}{2\pi} \sqrt{\frac{2 \times 5 \times 10^5}{\frac{12 \times 12}{24 \times 6.03 \times 10^{23}}}}$$

$$= 5.043 \times 10^{13} \text{ Hz}$$

$$\lambda = \text{wave number} = \frac{f}{c} = 1681 \text{ cm}^{-1}$$

Q Reduced mass of a diatomic molecule is $2.5 \times 10^{-26} \text{ kg}$ & its vibrational freq. is 2900 cm^{-1} . Calculate force constant.

Solⁿ

$$\text{Wave number } (\bar{\nu}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$2900 \times 10^5 \text{ m}^{-1} = \frac{1}{2 \times 3.14 \times 3 \times 10^8} \sqrt{\frac{k}{2.5 \times 10^{-23} \text{ g}}}$$

$$\therefore \sqrt{\frac{k}{2.5 \times 10^{-23}}} = 6 \times 3.14 \times 2.9 \times 10^{13}$$

$$\therefore k = \frac{3.73 \times 10^5 \text{ g/s}^2}{\text{g/s}^2}$$

$$= 7.46 \times 10^6 \text{ g/s}^2 \quad \checkmark$$

$$= 7.459 \times 10^5 \text{ g/s}^2 \quad \times$$

Q Force constant for carbon monoxide is
 Calculate the vibrational freq. if mass
 of carbon = $19.9 \times 10^{-27} \text{ kg}$
 oxygen = $26.6 \times 10^{-27} \text{ kg}$
 $f = 6.4 \times 10^{13} \text{ hz}$

⇒ Woodward - Fieser Rule.

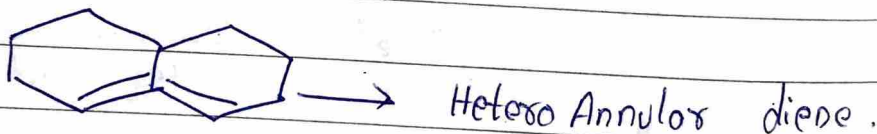
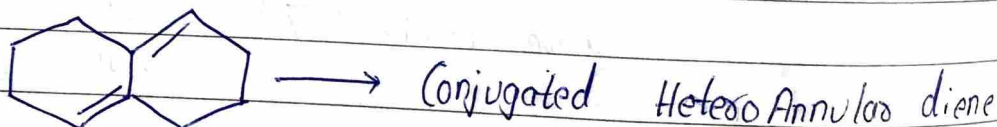
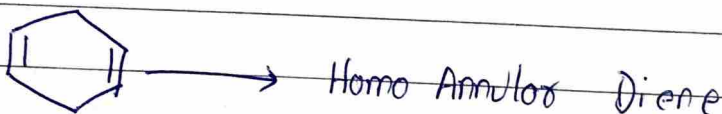
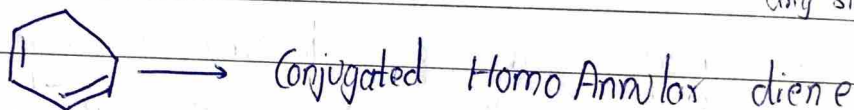
→ Applicable to ^{conjugated} diene, triene Alternate single & double bond.
 \downarrow
 $-C-C=C-C=C-$

1) Homo Annular diene

→ double bond must be inside the ring

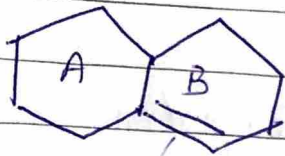
2) Hetero Annular Diene

→ double bond is outside the ring, (but it must be in any ring)



3) Endocyclic Bond ^{inside}

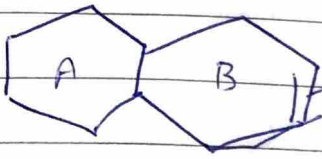
4) Exocyclic Bond. ^{outside}



This is shared

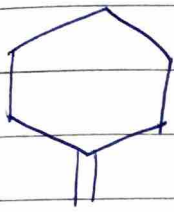
For ring B we can say that this bond is endocyclic bond.

For ring A we can say that the bond is exocyclic bond.

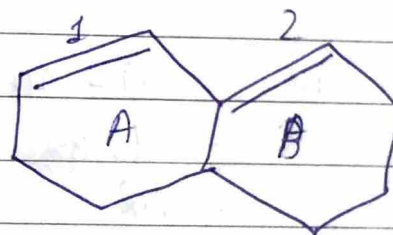


Bond is not shared, so we cannot say exo to any ring, but for ring B it is Endo

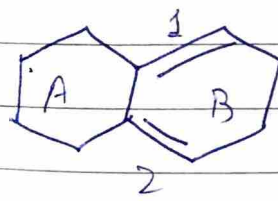
Q



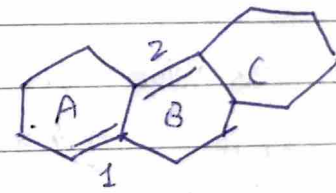
Exo
Not Homo, not
Hetero



Hetero
A → Exo to nothing
B → Exo to A
A, B → Endo



Homo
Endo Bonds → 2 (count)
Exo Bonds → 2 (count)
Bond 1 → Exo to A
Bond 2 → Exo to A



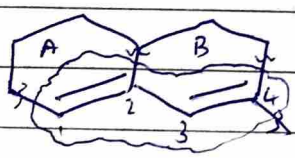
Hetero
Bond 1 → Exo to B
Bond 2 → Exo to A, C

$$\lambda_{max} = \text{Base Value} + \text{Summation of substituent contribution} + \sum \text{of other contribution} + \text{of sub.}$$

For

- 1) Homo Annular Diene, $\lambda_{max} = 253 \text{ nm}$
- 2) Hetero " " " " = 214 nm
- 3) Endo Cyclic Bond X
- 4) exo Cyclic Bond = 5 nm
- 5) Alkyl Substituent = 5 nm
- 6) Double Bond extending conjugation = 30 nm
- 7) Polar Gas - O-Alkyl = 6 nm
 - Cl, Br = 5 nm
 - NR₂ = 60 nm
 - OAc = 0 nm

1)



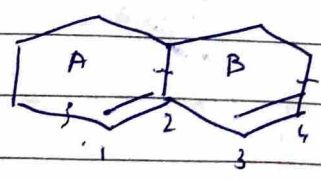
4 substituents are attached

Number 1 - 1 → Count
 Number 2 - 1
 Number 4 - 2
 + 4

Base Value = 214 nm → Cause Hetero.

+ 4 × 5 → Alkyl Substituent value
 + 5 → One exocyclic bond
 Total substituent

2)

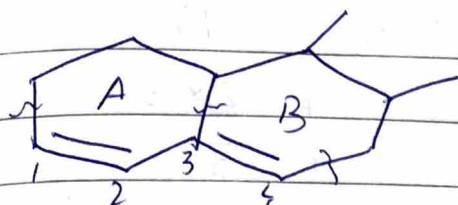


3 substituents

Base Value = 214 → Hetero

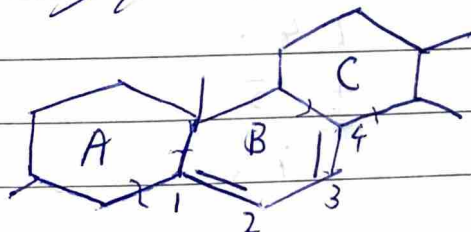
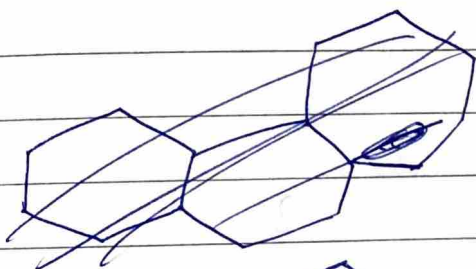
+ 3 × 5 → Alkyl
 + 5 → One exocyclic
 Count

3)



$$\begin{aligned} \lambda_{\max} \text{ Base Value} &= 214 \\ &+ 3 \times 5 \\ &+ 5 \end{aligned}$$

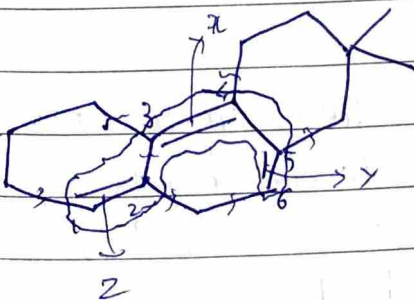
4)



Whenever there is homo or hetero, we will take homo because it has max^m value.

$$\begin{aligned} \lambda_{\max} &= 253 \\ &+ 4 \times 5 \\ &+ 10 \longrightarrow 2 \text{ exocyclic bond} \\ &= 283 \end{aligned}$$

5)



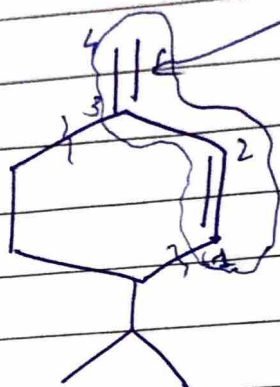
$$\begin{aligned} \lambda_{\max} &= 214 \\ &+ 6 \times 5 \\ &+ ((2 \times 5) + (1 \times 5)) \\ &+ (1 \times 5) \end{aligned}$$

α -bond \rightarrow λ bond

2-bond Exo

$= 264$

6)



$$\lambda_{max} = 253$$

$$\lambda_{max} = 214$$

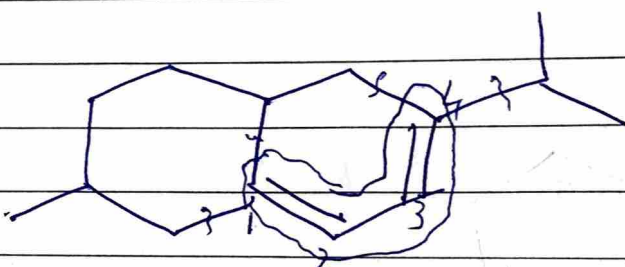
$$+ 2 \times 5$$

$$+ 5$$

One exocyclic

$$229$$

7)



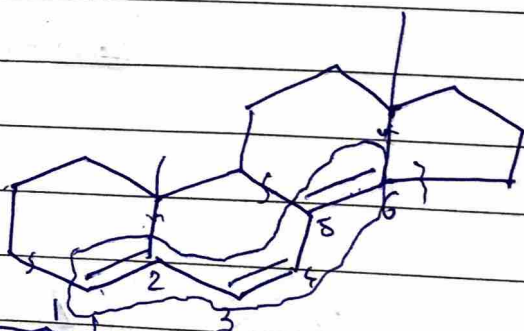
$$\lambda_{max} = 253$$

$$+ 4 \times 5$$

$$+ 5$$

$$278$$

8)

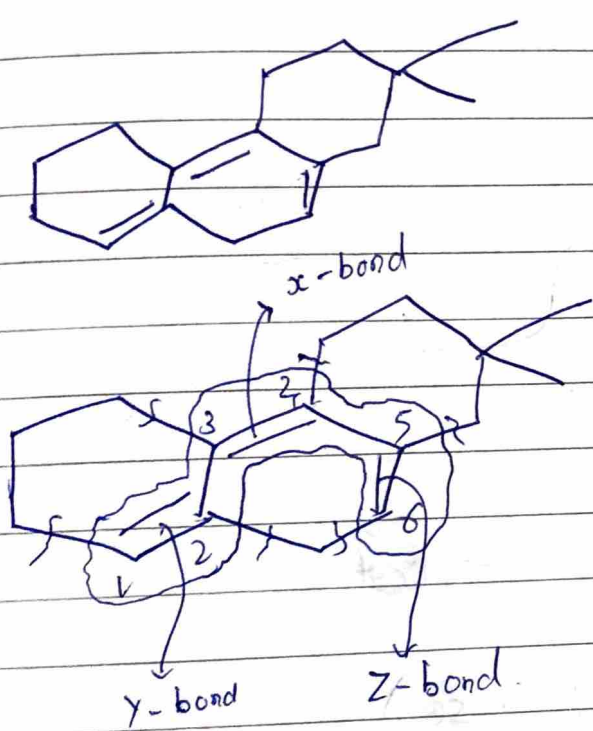


Here more than 2 double bonds are there so we will use double bond extended conjugation

$$\begin{aligned}
 \lambda_{max} &= \text{Hetero} \quad 214 \\
 &+ 30 \quad \rightarrow \text{double bond extended} \\
 &+ 5 \times 5 \\
 &+ \underline{3 \times 5} \\
 &\quad \underline{279} \quad 284
 \end{aligned}$$

5)

Solⁿ



$$\begin{aligned}
 \lambda_{max} &= 253 \\
 &+ 30 \\
 &+ 6 \times 5 \\
 &+ 4 \times 5 \\
 &\quad \underline{333} \\
 &\quad \left(\begin{array}{l} 2 \text{ for } x\text{-bond} \\ 1 \text{ for } y\text{-bond} \\ 1 \text{ for } z\text{-bond} \end{array} \right)
 \end{aligned}$$