~~Nil~~

⇒ 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 : $A = \varepsilon CL$

- ε → Epsilon (Molar Absorptivity)
- L → pathlength
- C → concentration

(Molar Absorptivity)

pathlength $L = 1\ cm$

Epsilon $\varepsilon = 40.9$

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

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

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

1) Molar Absorptivity of soln
2) Absorbance if the conc^n is 0.65 M
3) Concentration if absorbance is 0.450.

Soln

1) $A = \varepsilon CL$

$0.075 = \varepsilon \times 0.25 \times 1$

$\therefore \quad \varepsilon = 0.3\ M^{-1} cm^{-1}$

↳ It is same for soln

2) $A = \varepsilon CL$

$= 0.3 \times 0.65 \times 1$

$= 0.195$

3) $A = \varepsilon CL$

$0.45 = 0.3 \times C \times 1$

$\therefore \quad C = 1.5\ M$

Date: YOUVA

Q Intensity of incident light on an sample is 0.5 w/m² & the intensity of light entering the detector is 0.36 w/m². Calculate the transmittance & absorbance.

Ans

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

$$= +\log \frac{0.5}{0.36} \qquad = 0.72$$

$$= +0.143$$

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

Soln

$A = \varepsilon C L$ $\quad L = 3cm \quad \varepsilon = 4000$ $\quad C = ?$

$$A = -\log T$$
$$= 0.523$$

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

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

1) A
2) Molar Absorpitivity
3) % T of 2×10^{-5} M soln in 4cm cell.

Soln ~~A = ECL~~

=

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

2) $A = \varepsilon CL$

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

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

$= 8.7 \times 10^{3} = 8737.5\ M^{-1}$

3) $A = \varepsilon CL$

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

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

$T = 10^{-0.696}$

$= 0.2013$

Q Thickness 2 cm
Transmitted light is 0.12 times of incident light, Molar Absorpitivity is 0.35 $M^{-1}cm^{-1}$. Calculate the conc^{n} & absorbance

Soln $A = \varepsilon CL$

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

$= 0.92$

$C = \frac{A}{\varepsilon L} = \frac{0.92}{0.35 \times 2} = 1.3\ M$

Q A sol^{n} of thickness 4 cm, transmits 40%. Calculate con^{n} of sol^{n} whose molar absorpitivity is 4000 $dm^{3}\ mol^{-1}\ cm^{-1}$ at 280 nm.

Sol:

$$A = \varepsilon C L$$

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

⇒ U-V Spectrophotometer. (spectrometer)

→ To measure the spectrum of compound.

→ In reference cuvett 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 ~~f~~. Calculate wavelength

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

If $f = 810$ kHz, $\lambda = 370.37$ m

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

Soln $\lambda = 0.045$ ~~cm~~ m

$f = 6.6 \times 10^9$ ~~Hz~~ Hz

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

If bond strength = x for C-C

= 2x " C=C

= 3x " C≡C

Q Calculate C-H bond freq.

$k = 5 \times 10^5$ gm/sec²

mass of carbon = 20×10^{-24} g

" " hydrogen = 1.6×10^{-24} g

Soln $f = \frac{1}{2\pi}\sqrt{\frac{5\times10^5}{\frac{3.2\times10^{-47}}{21.6\times10^{-24}}}} = 9.24 \times 10^{13}$ Hz

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

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

Q Calculate the wave number of stretching vibration for C=C.

Soln

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

$$\frac{12 \times 12}{24 \times 6.03 \times 10^{23}} = \frac{10^{23}}{12.06}$$

For double bond

$$= \frac{1}{2\pi}\sqrt{\frac{2 \times 5 \times 10^5}{\frac{12 \times 12}{24 \times 6.023 \times 10^{23}}}}$$

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

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

Q Reduced mass of a diatomic molecule is 2.5×10^{-26} kg & its vibrational freq. is obt. at 2900 cm^{-1}. Calculate force constant.

Soln

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

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

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

$$\therefore k = 7.459 \times 10^5 \ g/s^2$$

= 7.46 x 10^6 g/s^2 ✓ ✗

convert this from kg to gm

Q Force constant for carbon monoxide is 1860 Calculate the vibrational freq. if mass of carbon = 19.9×10^{-27} kg
oxygen = 26.6×10^{-27} kg

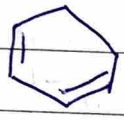
f = 6.4 x 10^11 hz

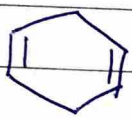
⇒ Woodward - Fieser Rule.

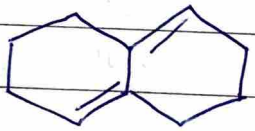
→ Applicable to conjugated diene, triene → Alternate single & double bond.

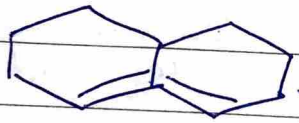
$-C-C=C-C=C-$

- 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

 → Conjugated Homo Annular diene

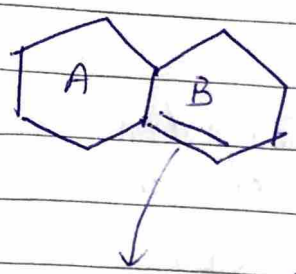
 → Homo Annular Diene

 → Conjugated Hetero Annular diene

 → Hetero Annular diene.

3) Endocyclic Bond → Inside

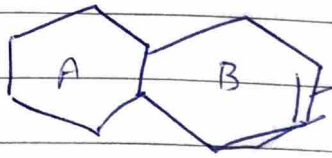
4) Exocyclic Bond. → Outside



This is shared

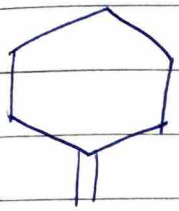
For ring B we can say that this bond is endocyclic bond.

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



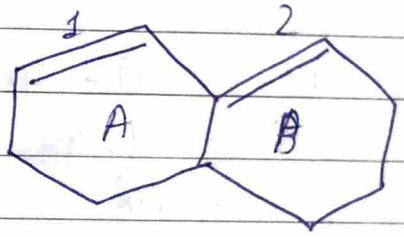
→ Bond is not shared, so we cannot say exo to any ring, but for ring B it is Endo

Q



Exo

Not Homo, nd Hetero

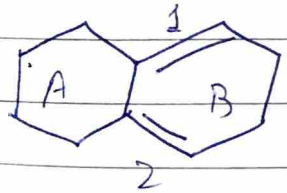


Hetero

A → Exo to nothing

B → Exo to A

A, B → Endo



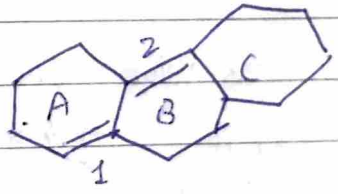
Homo

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

λ_{max} = Base Value + Summation of substituent contribution

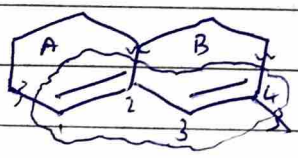
+ Σ of other contribution ~~+ Σ of such,~~

For

1) Homo Annular Diene, λ_{max} = 253 nm
2) Hetero " " " = 214 nm
3) Endo Cyclic Bond ×
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
- NR_2 = 60 nm
- OAc = 0 nm.

1)



4 substituents are attatched

Number 1 - 1 → Count
Number 3 - 1
Number 4 - 2
+ 4

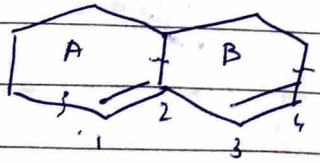
Base Value = 214 nm → Cause Hetero.

+ 4 × 5 → Alkyl Substituent value

Total substituent

+ 5 → One exocyclic bond

2)



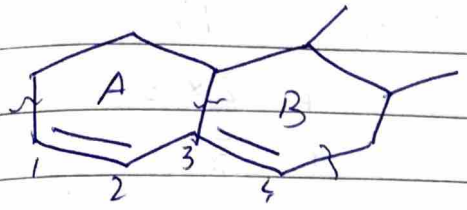
3 substituents

~~Cause~~ Base Value = 214 → Hetero

Count ← + 3 × 5 → Alkyl

+ 5 → One exocyclic

3)



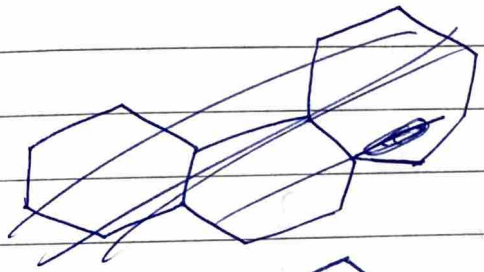
λ_{max}

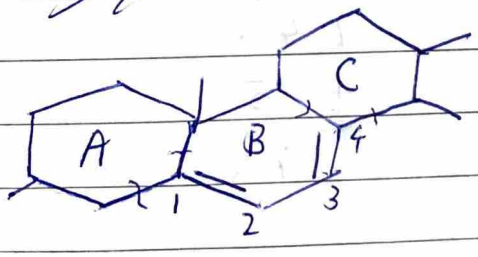
~~Base Value~~ = 214

+ 3 × 5

+ 5

4)





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

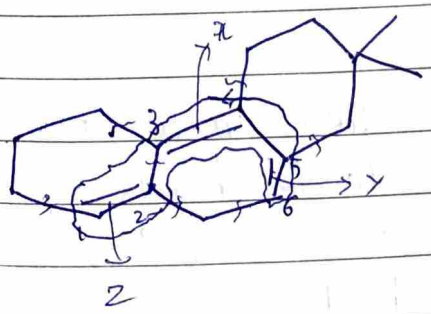
λ_{max} = 253

+ ~~4~~ × 5

+ 10 → 2 exo cyclic bond

~~283~~ 283

5)



λ_{max} = 214

+ 6 × 5

+ ((2 × 5) + (1 × 5)) + (1 × 5)

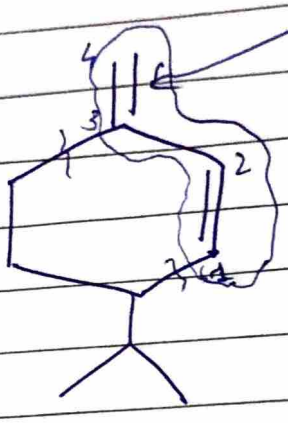
2-bond exo

x-bond

y bond

= ~~264~~ 264

6)



~~λ_{max} 253~~

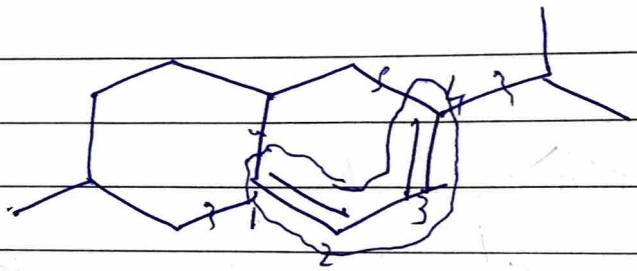
$\lambda_{max} = 214$

$+ 2 \times 5$

$+ 5$ → One exocyclic

229

7)



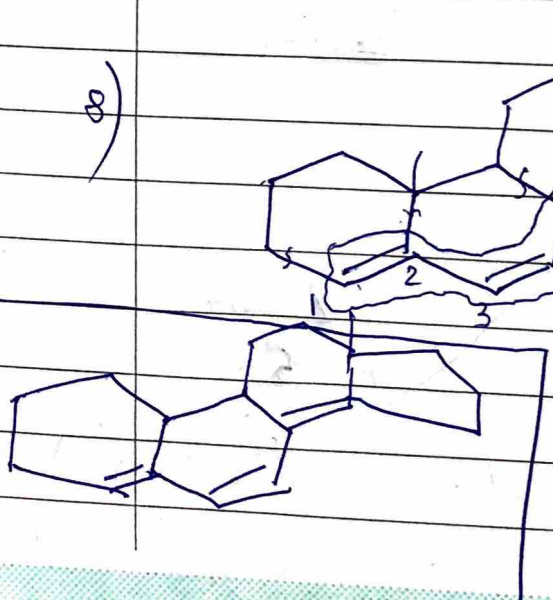
$\lambda_{max} = 253$

$+ 4 \times 5$

$+ 5$

278

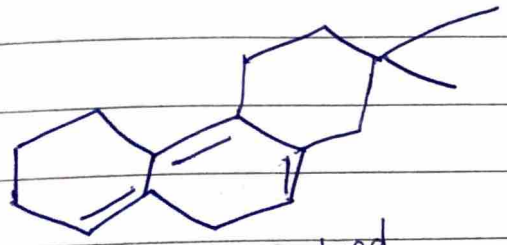
8)



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

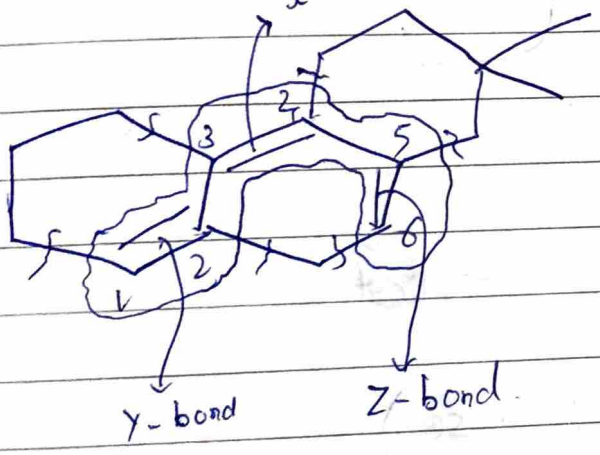
λ_{max} = Hexa 214
+ 30 → double bond extended
+ 5 × 5
+ ~~3~~ × 5
~~279~~ 284

5)



λ_{max}

Soln



λ_{max} = 253
+ 30
+ 6 × 5
+ 4 × 5
333

(2 for x-bond
1 for y-bond
1 for z-bond)