~~Nu~~

$\Rightarrow$ Numericals

Q Solution of thickness 1 cm, molar absorpitivity = 40.[illegible] at 290 nm. If the absorbance is 0.111. Calculate concentration.

Soln. Lambert's law :- $A = \epsilon C L$

Epsilon (Molar Apsorpitivity)

pathlength

concentration

Molar Absorptivity

pathlength $L = 1cm$

Epsilon $\epsilon = 40.9$

$A = \epsilon C L$ $\therefore$ $0.111 = 40.9 \times C \times 1$

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

Q 0.25 M soln, pathlength = 1 cm, absorbance = 0.07[illegible] at 560 nm. Calculate

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

Soln 1) $A = \epsilon C L$

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

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

$\hookrightarrow$ It is same for soln

2) $A = \epsilon C L$

$= 0.3 \times 0.65 \times 1$

$= \cancel{1.95}$ 0.195

3) $A = \epsilon C L$

~~A~~ $0.45 = 0.3 \times C \times 1$

$\therefore$ $C = 1.5 M$

YOUVA

Date:

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

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

$= \boxed{0.72}$

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

$\boxed{= +0.143}$

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

$A = \varepsilon C L$

$L = 3cm$ $\varepsilon = 4000$
$C = ?$
$\cancel{A =}$

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

$\therefore$ $C = \frac{0.523}{4000 \times 3} = 4.35 \times 10^{-5}$ mol/dm³

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) $A = \varepsilon CL$

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

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

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

3) $A = \varepsilon CL$

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

$\therefore -\log T = 0.696$

$T = 10^{-0.696}$

$= 0.2013$

Q Thickness 2 cm

Transmitted light is 0.12 times of incident light, Molar Absorpitivity is 0.35 $M^{-1} cm^{-1}$. Calculate the concn & 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 soln of thickness 4 cm, transmits 40%, Calculate conn of soln whose molar absorpitivity is 4000 $dm^3\ mol^{-1}\ cm^{-1}$ at 280 nm.

M	T	W	T	F	S	S

Page No.:
Date:
YOUVA

Sol^n

$$A = \varepsilon C L$$

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

⇒ U-V Spectrophotometer. (spectrometer)

→ To measure the spectrum of compound.

→ In reference cuvett absorbance is 0.
↳ device.

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

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

Sol^n $\lambda = \frac{c}{f} = \frac{300}{95} \doteq 3.158 \text{ m}$

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

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

Sol^n $\lambda = 0.045$ ~~cm~~ m

$f = 6.6 \times 10^9$ ~~m~~ 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.
$k = 5 \times 10^5 \text{ gm/sec}^2$
mass of carbon = 20×10^{-24} g
" " hydrogen = 1.6×10^{-24} g

Sol^n $f = \frac{1}{2\pi}\sqrt{\frac{5 \times 10^5}{\frac{3.2 \times 10^{-47}}{21.6 \times 10^{-24}}}}$ = ~~$\times 10^{9}$~~

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

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

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

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

Sol^n

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

$\cancel{\frac{12\times 12}{\frac{24}{2}\times 6.03\times 10^{23}}}$ $\cancel{\frac{10^{23}}{12.06}}$

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.

Sol^n

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

$$2.9\times 10^{5}\,m = \frac{1}{2\times 3.14\times 3\times 10^{8}}\sqrt{\frac{k}{2.5\times 10^{-23}\ g}}$$

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

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

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

Page No
Date

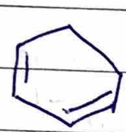
Q Force constant for carbon monoxide is 18..
Calculate the vibrational freq. if mass
of carbon = 19.9×10^{-27} kg
oxygen = 26.6×10^{-27} kg

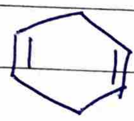
⇒ WoodWard - Fieser Rule.

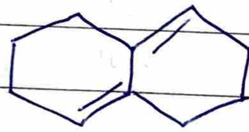
→ Applicable to conjugated diene, triene → Alternate single & double bond.

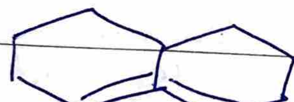
$-C-C=C-C=C-$

→ 1) HomoAnnular 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

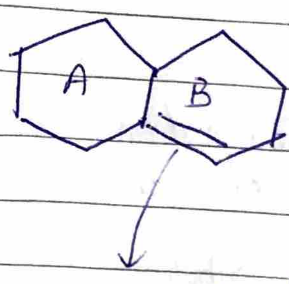
 → Conjugated Homo Annular diene

 → Homo Annular Diene

 → Conjugated Hetero Annular diene

 → Hetero Annular diene.

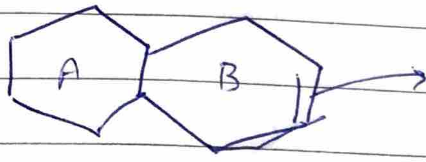
3) Endocyclic Bond → Inside
4) Exocyclic Bond. → Outside



This is shared

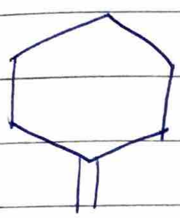
For ring B we can say that this bond is endocyclic bond.

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

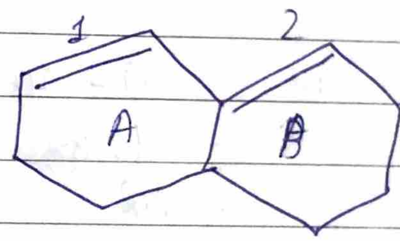


Bond is not shared, so we cannot say exo to any ring, but for ring B it is Endo

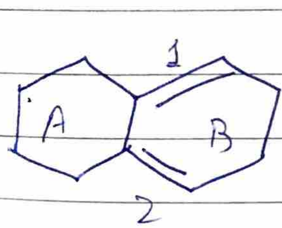
Q



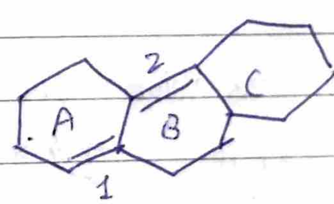
Exo
Not Homo, not Hetero



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

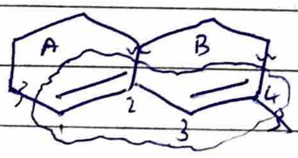
λ_{max} = Base Value + Summation of substituent contribution

+ Σ of ~~other contribution + Σ of sub.~~

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 attached

Number 1 - 1 → count

~~Number 2~~ - 1

Number 4 - 2

+ 4

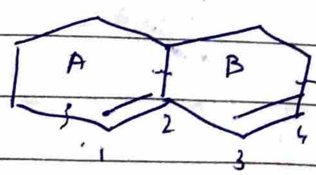
Base Value - 214 nm → Cause Hetero.

+ 4 × 5 → Alkyl Substituent value

Total substituent

+ 5 → One exocyclic bond

2)



3 substituents

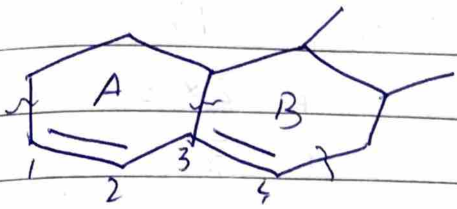
~~Base~~ Base Value = 214 → Hetero

+ 3 × 5 → Alkyl

Count

+ 5 → One exocyclic

3)

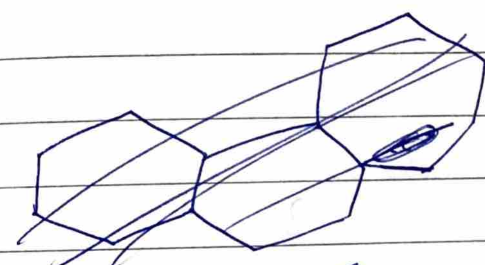


λ_{max} ~~Base Value~~ $= 214$

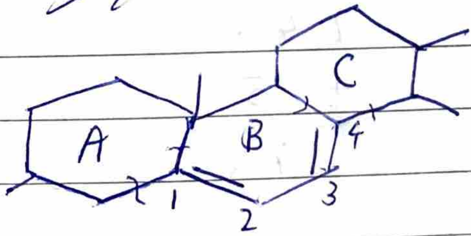
$+ 3 \times 5$

$+ 5$

4)



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



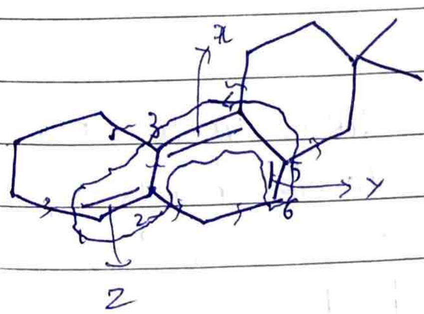
$\lambda_{max} = 253$

$+ 4 \times 5$

$+ 10$ → 2 exo cyclic bond

~~283~~ 283

5)



$\lambda_{max} = \cancel{2}\ 214$

$+ 6 \times 5$

$+ \left((2 \times 5) + (1 \times 5) + (1 \times 5) \right)$

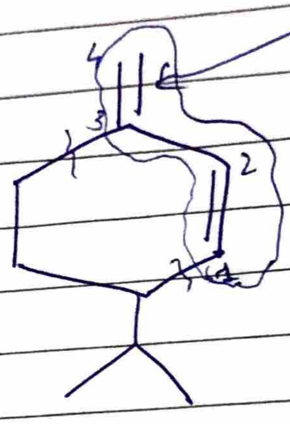
z-bond ~~exo~~

x-bond

y bond

$= \cancel{264}$ 264

6)

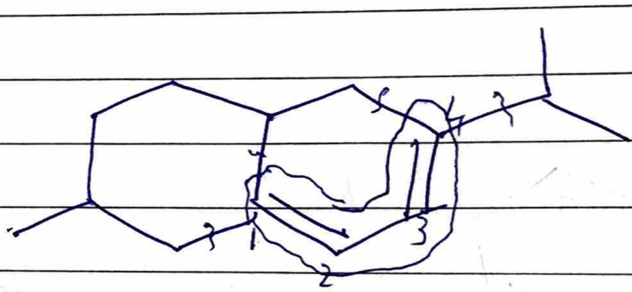


~~λ_{max} = 253~~

~~+ 1~~

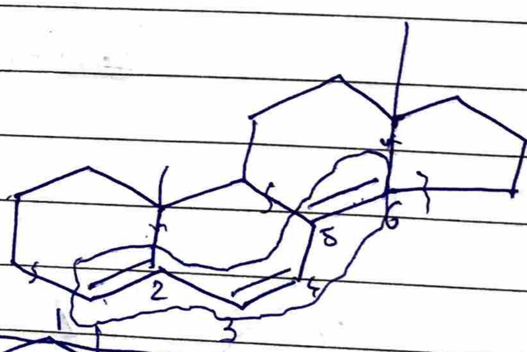
$$\lambda_{max} = 214$$
$$+\ 2 \times 5$$
$$+\ 5 \rightarrow \text{One exocyclic}$$
$$\overline{\ 229\ }$$

7)

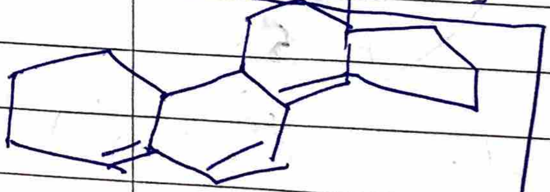


$$\lambda_{max} = 253$$
$$+\ 4 \times 5$$
$$+\ 5$$
$$\overline{\ 278\ }$$

8)

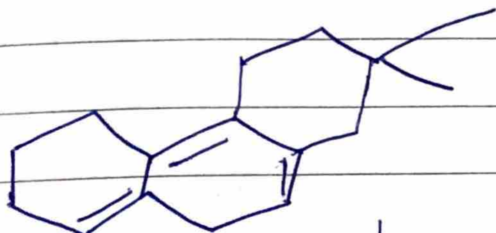


Here more than 2 double bonds are there so we will use double bond extended conjugation

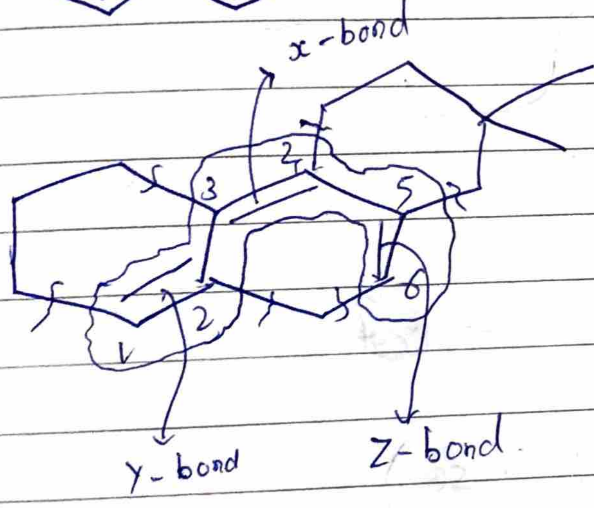


M T W T F S S
Page No.:
Date:
YOUVA

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

5) 

λ_{max}

Sol^n 

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

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