

Absorption and Intensity Shifts

Absorption Shift

Bathochromic shift (or Red shift) :-
 It is an effect by virtue of which the absorption maximum is shifted towards longer wavelength due to the presence of auxochrome or by change of solvent.

auxochrome $\xrightarrow{\text{chromophore}}$ longer λ . (Red)

Hypsochromic shift or effect (or Blue shift)
 It is an effect by virtue of which the absorption maximum is shifted towards shorter wavelength

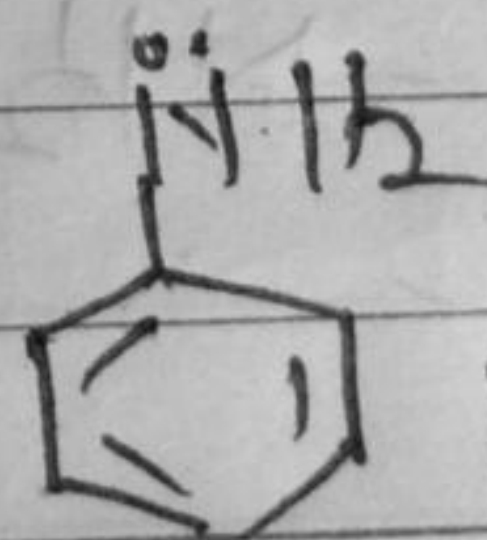
shorter \leftarrow chromophore subtraction of conjugation (Blue)

* It may be caused by the removal of conjugation and also by changing the polarity of the solvent



conjugation of π - π on π -atom

$\lambda = 280 \text{ nm}$
 Non acidic solution



Acidic solⁿ

$\lambda = 203 \text{ nm}$
 (No conjugation of π on N-atom)

Intensity shift

Hyperchromic effect :- which
it is an effect due to ^{which} intensity of absorption
maximum increases i.e., ϵ_{max} increases.

ex

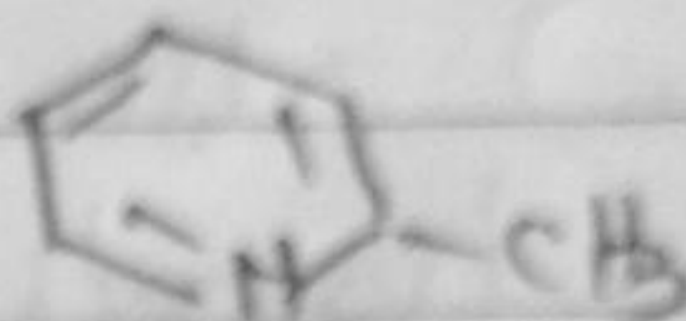


pyridine

for B-band

$$\lambda = 257 \text{ nm}$$

$$\epsilon_{max} = 2750$$



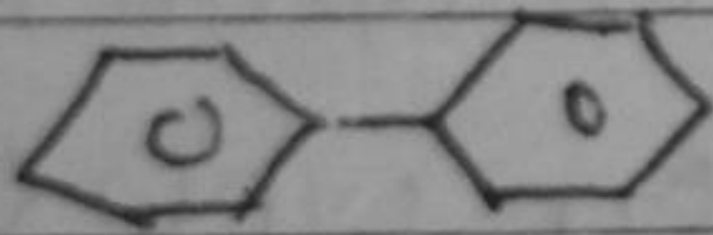
2-methylpyridine

$$\lambda = 262$$

$$\epsilon_{max} = 3560$$

The introduction of ^{an} auxochrome ^{and} increased
conjugation results increased intensity.

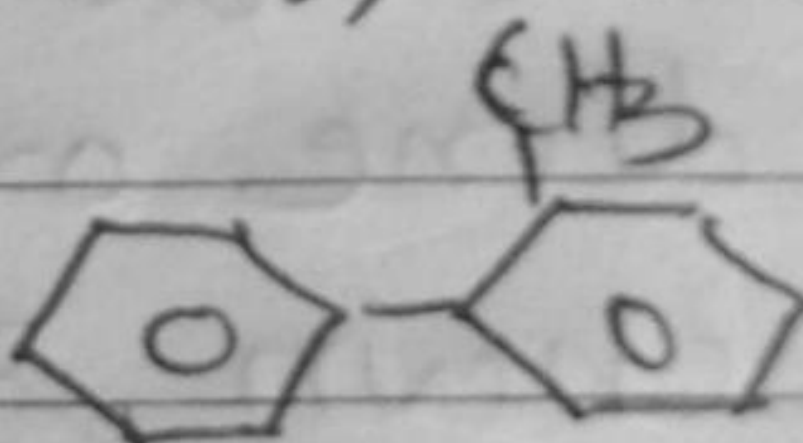
Hypochromic effect :- it is defined as an
effect due to which the intensity of absorption
maximum decreases. i.e., ϵ_{max} decreases.



Biphenyl

$$\lambda = 250 \text{ nm}$$

$$\epsilon_{max} = 19000$$



2-methylbiphenyl

$$\lambda = 237 \text{ nm}$$

$$\epsilon_{max} = 1050$$

The introduction of the gro which distort
the geometry of the molecule causes
hypochromic effects.

maximum in Dienes:
(calculation of UV absorption wavelength
in conjugated Dienes and Trienes)

Woodward formulated certain empirical rules for calculating the λ_{max} in case of diene. These rules are modified by Fieser in 1948. According to these rules, each type of diene has a certain fixed basic value and the value of absorption maximum (λ_{max}) depends upon:

- (i) the number of alkyl substituents ring residue on double bond.
- (ii) The number of double bonds which extend conjugation and
- (iii) The presence of polar group such -Cl, -Br, -OR, -SR etc.

Woodward and Fieser rules for calculating absorption maximum in case of dienes and trienes are given in table below -

λ_{max} (nm) (K-band)

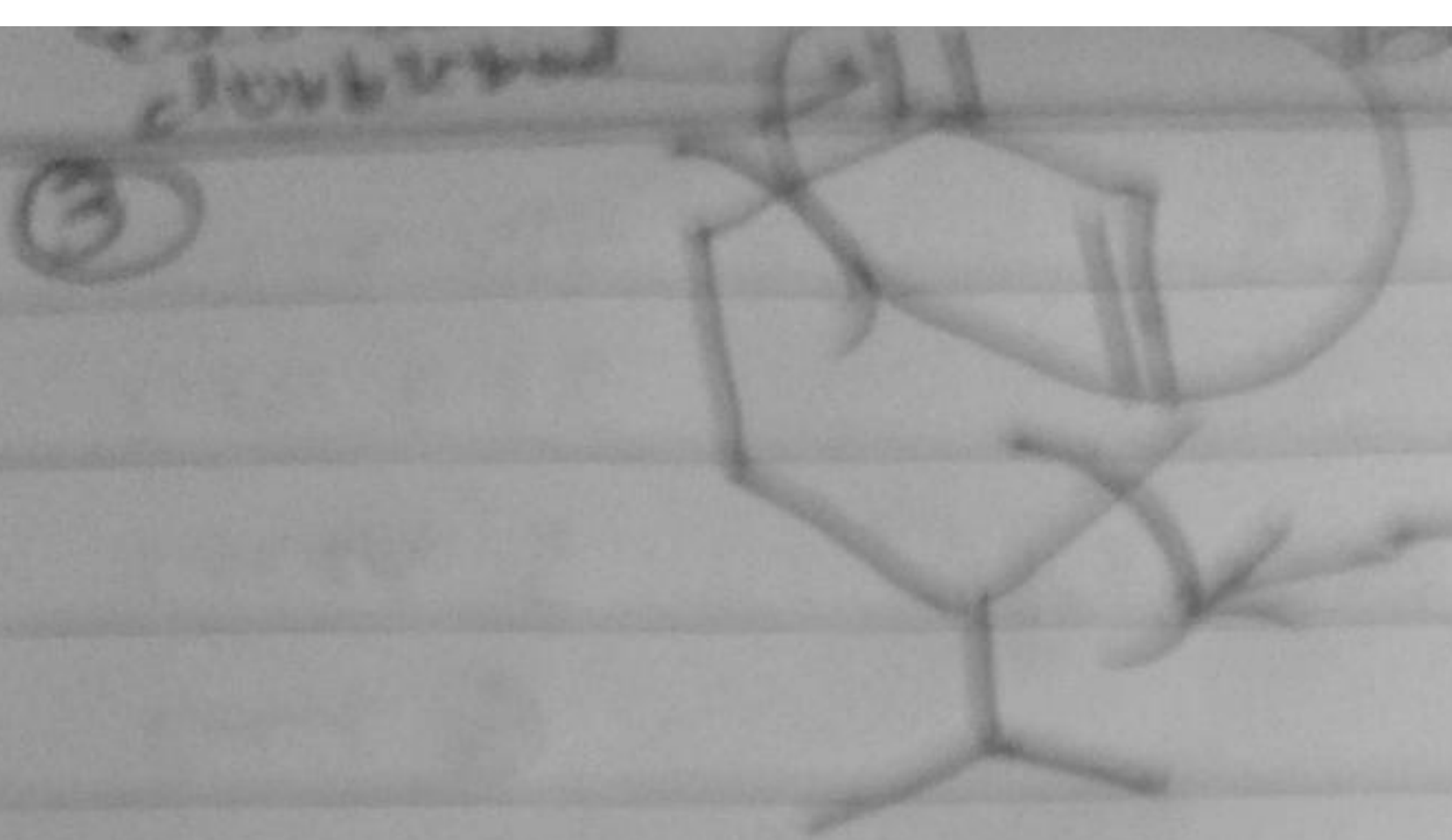
Parent value for Butadiene or acyclic conjugated diene	217 nm
Acyclic triene	245 nm
Homocyclic conjugated diene	253 nm
Heterocyclic	215 nm

Addition (or increment) for each substituent

Alkyl substituent or ring residue	+5 nm
Exocyclic double bond	+5 nm
Double bond extending conjugation	+30 nm

Auxochrome

-OR	+6 nm
-SR	+30 nm
-Cl, -Br	+5 nm
-NR ₂	+60 nm
-COCH ₃	0 nm



Two carbons substituted on ring residue

β -phellandrene

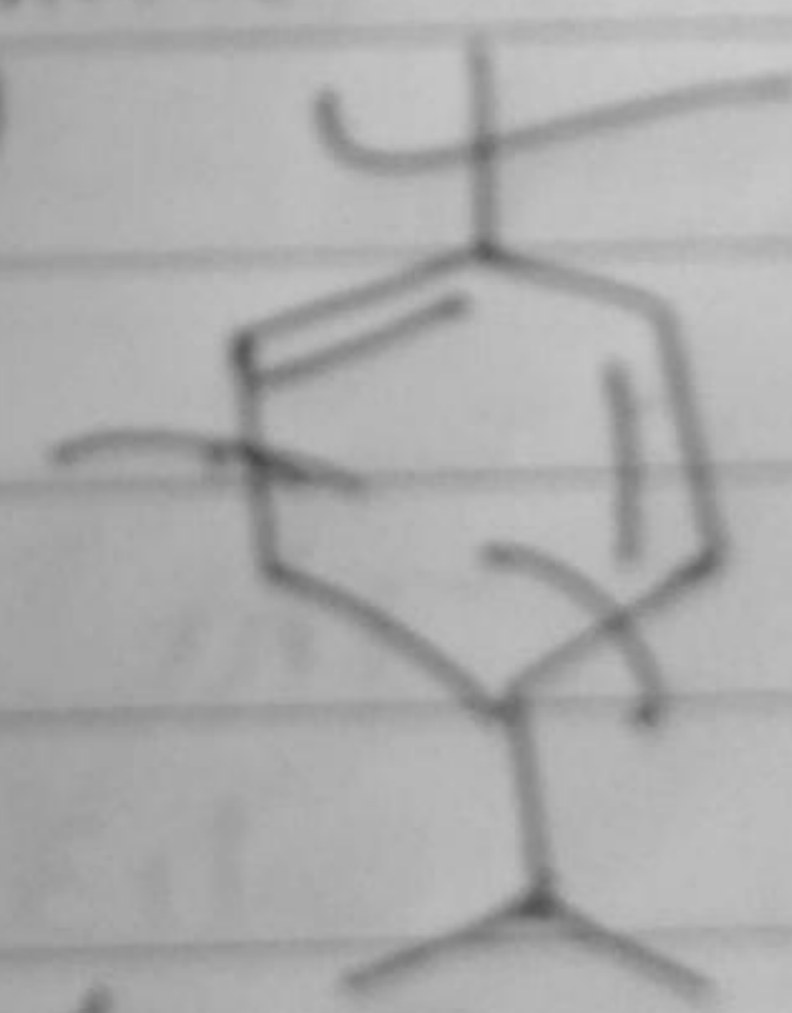
$$\begin{aligned} \lambda_{max}^{cal} &= 214 \text{ - Base value} \\ &+ 45 \text{ (1-6 cyclo double bond)} \\ &+ 10 \text{ (5x2=10 carbons substituted)} \\ \hline &299 \text{ nm} \end{aligned}$$

①

$$\lambda_{max}^{obs.} = 232 \text{ nm.}$$



Base (Homocyclic diene)



α -terpinene
 α -terpinene

α -phellandrene

$$\begin{aligned} \lambda_{max}^{cal} &= 253 \text{ Base value} \\ &+ 20 \text{ (5x4 allyl substitution)} \\ \hline &273 \text{ nm} \end{aligned}$$

$$\begin{aligned} \lambda_{max}^{cal} &= 253 \text{ (Base)} \\ &+ 15 \text{ (3-ol substit)} \\ \hline &268 \text{ nm} \end{aligned}$$

obs

$$\lambda_{max}^{obs.} = 263 \text{ nm}$$