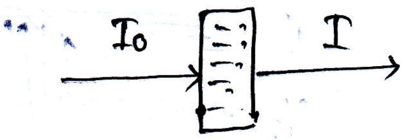
Ultraviolet - visible spectroscopy

Visible region : 400 nm – 780 nm
Near UV region : 200 – 400 nm
Far UV region : below 200 nm

Absorption Laws and Molar Absorptivity ⇒



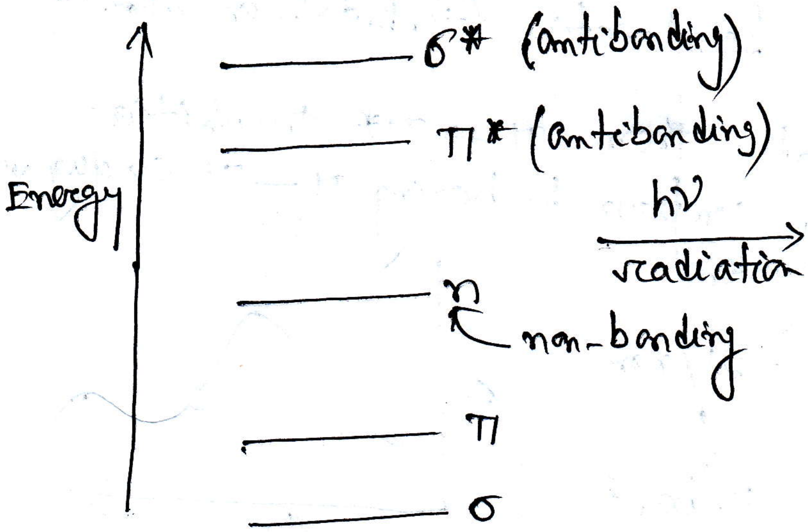
I_0 = intensity of incident radiation
I_0 = intensity of transmitted radiation

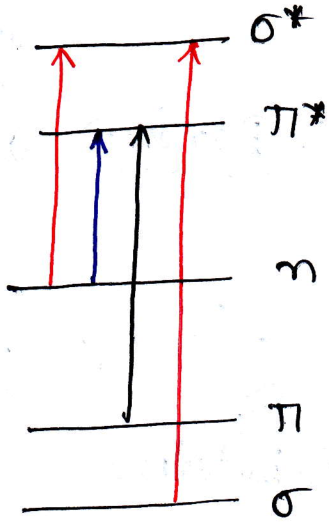
Lambert - Beer law ⇒

$$\log_{10} I_0/I = \epsilon . c . l = A$$

A = absorbance , c = concentration (mole/Lit.)
l = path length of the sample (cm)
ϵ = molar absorptivity (depends only on temp, wave length and the specific compound)
⇓
molar extinction coefficient

Principle of absorption ⇒ Electronic transition between occupied and unoccupied Molecular Orbitals.

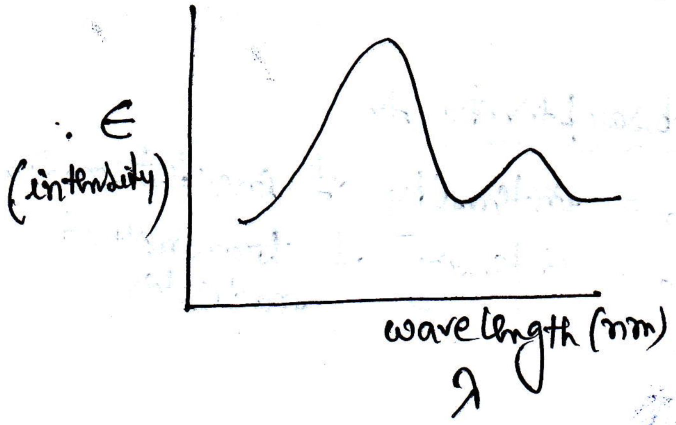




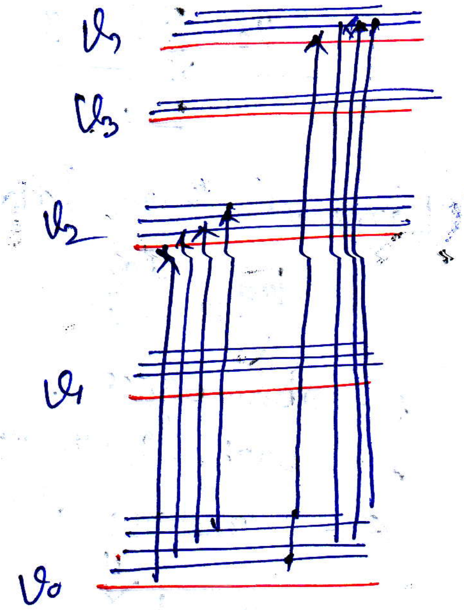
$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi - \pi^* > n \rightarrow \pi^*$$

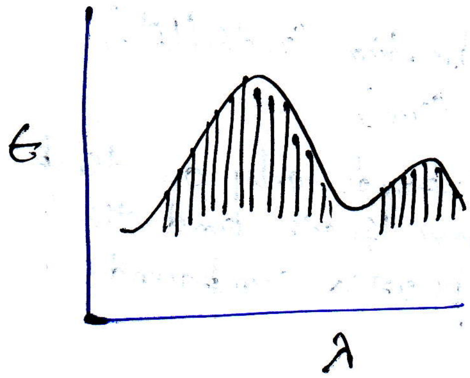
$\sigma \rightarrow \sigma^*$ (120 – 200 nm) [Vacuum region]

Appearance of UV-VIS spectrum



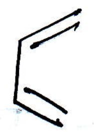
⇐ absorption band





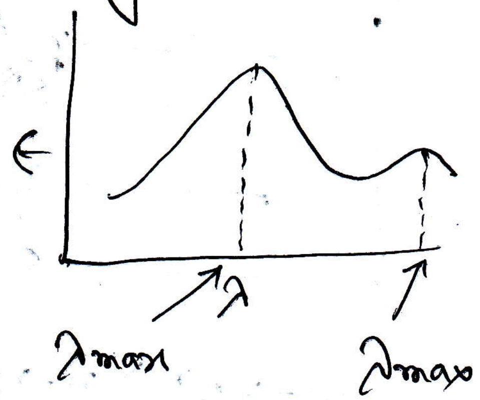
ε ⇒ depends on probability of transition
geometry of orbitals
Symmetry of orbitals
quantum restriction (forbidden or allowed)

K-Bands ⇒ originate from $\pi \rightarrow \pi^*$ transition in compounds having $\pi - \pi$ conjugated system

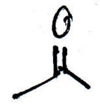


1,3-butadiene

⇒ λ_{max} = 217 nm
↑
K-band

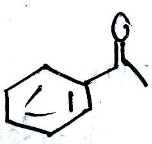


R-Bands ⇒ Originate from $n \rightarrow \pi^*$ transition (forbidden bands $\epsilon < 100$)

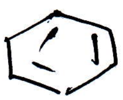

acetone ⇒ λ_{max} 279 nm

B-Bands ⇒ (benzenoid band) Originate from $\pi \rightarrow \pi^*$ transition in aromatic System


λ_{max} 256


λ_{max} 278

E-Bands ⇒ (ethylenic band) → E_1-band (shorter λ_{max}, more intense); → E_2-band (longer wavelength, low intensity)


$\left.\begin{matrix}\lambda_{max}\ 180 \\ (\epsilon\ 60{,}000)\end{matrix}\right\} E_1$

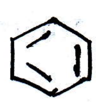
$\left.\begin{matrix}\lambda_{max}\ 200\ nm \\ \epsilon = 7900\end{matrix}\right\} E_2$

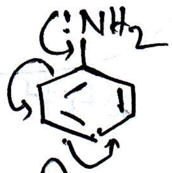
Chromophore ⇒ Any group responsible for imparting (UV-VIS absorption) colour to a compound.

Examples : $C=C$, $C\equiv N$, $C\equiv C$, $C=O$, $N=N$

Auxochrome ⇒ An auxochrome is a substituent on a chromophore which enhances colour imparting property of the chromophore

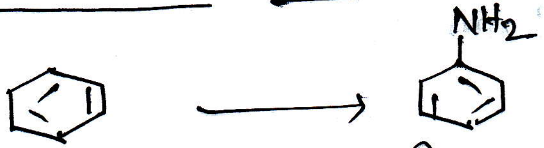
additional delocalization ⇒


λ_{max} 256 nm
$\epsilon = 200$


λ_{max} 280 nm
ϵ 1430

Shifts

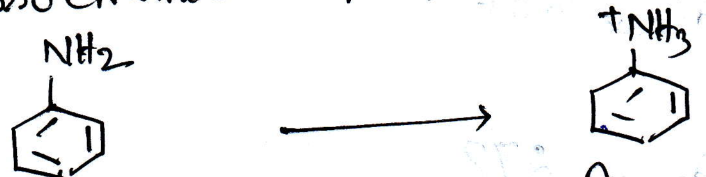
1. Bathochromic Shift (Red Shift) [Cause ⇒ ?]



λmax 256 nm → λmax 280 nm

→ shift towards longer wavelength

2. Hypsochromic Shift (Blue shift) [Cause ⇒ ?]



λmax 280 nm → λmax 254 nm

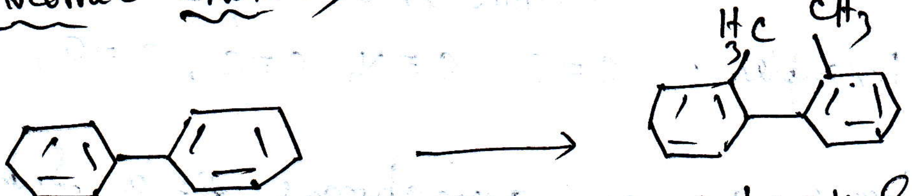
→ shift towards shorter wave length

3. Hyperchromic Shift ⇒ [Cause ⇒ ?]

ε = 200 → ε = 1230

→ Shift towards higher ε value

4. Hypochromic Shift ⇒



biphenyl → 2,2'-dimethyl biphenyl

λmax 252 nm → λmax 270 nm

ε = 19000 → ε = 800

shift towards lower ε value

Factors affecting λ_{max} value and ϵ value ⇒

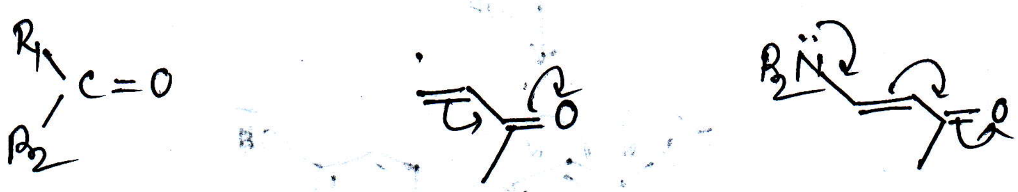
λ_{max} ⇓ extent of conjugation

ϵ value ⇓

$$\epsilon = 0.87 \times P \times a$$

p = transition probability

a = area of chromophore

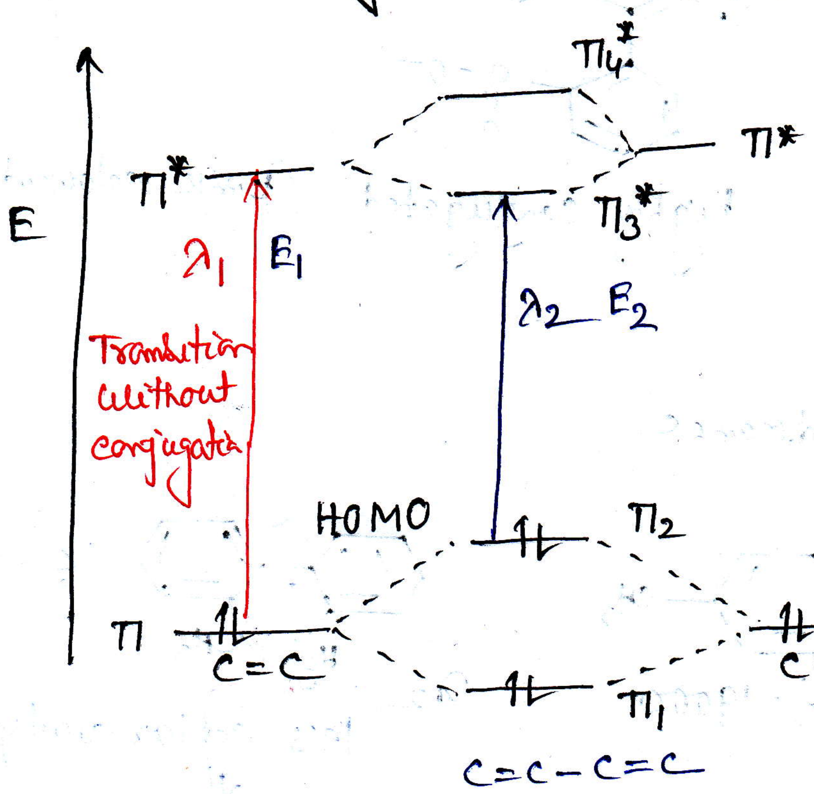


⟶ area of chromophore increases

⟶ λ_{max} value increases

⟶ ϵ value increases

Effect of conjugation ⇒

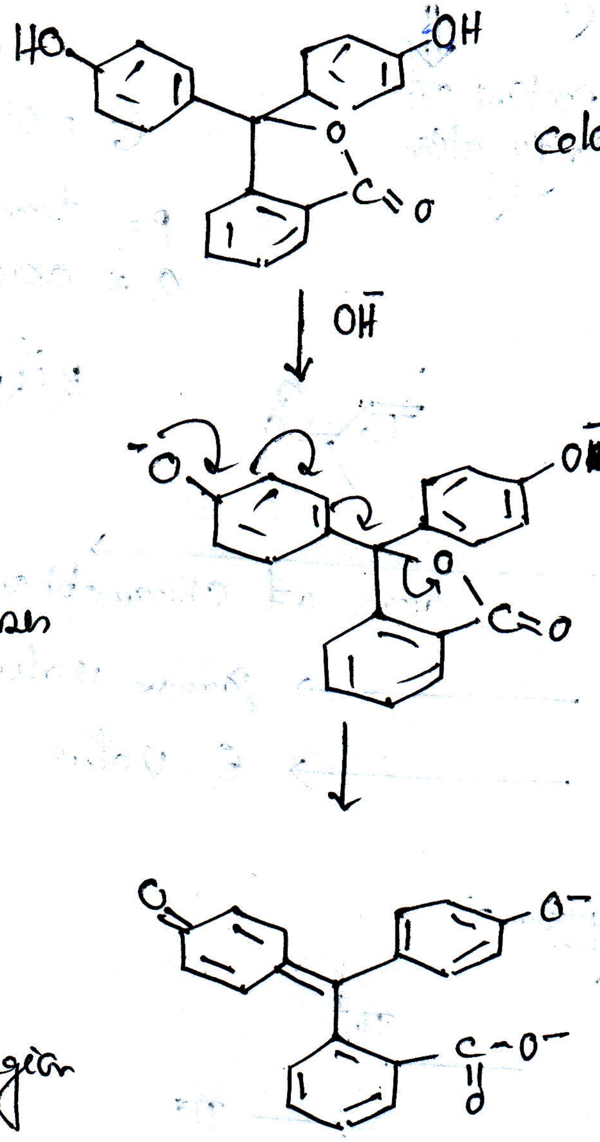


$E_2 < E_1$

$\lambda_2 > \lambda_1$

Why phenolpthalein shows pink colouration in alkaline medium?

λmax
UV-region
colourless



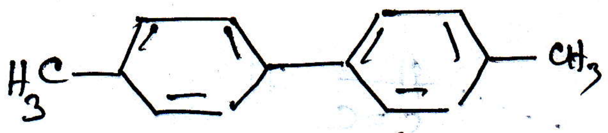
colourless

conjugation increases

λmax
visible region

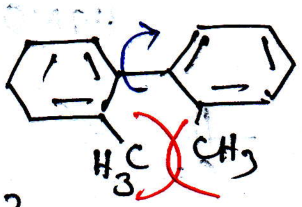
highly conjugated (pink colouration)

Effect of steric hindrance



$\Downarrow$ $\epsilon = 19000$

λ_1 co-planar



$\epsilon = 800$

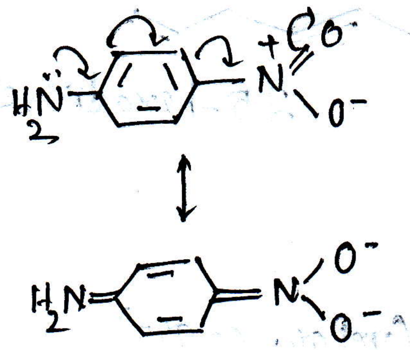
λ_2

less coplanarity
$\Downarrow$
less conjugation
$\Downarrow$
λmax decrease

$\lambda_1 > \lambda_2$

Problem} How to distinguish between m-nitro aniline and para nitroaniline?

λ_1



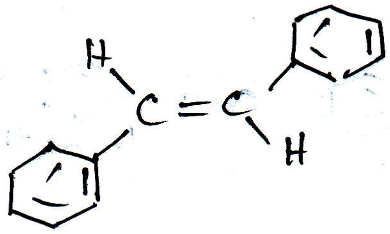
λ_2

no extension of conjugation

conjugation increases

$\lambda_1 > \lambda_2$

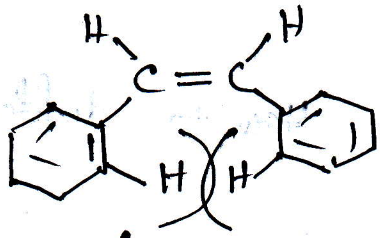
Problem} How to differentiate cis- and trans-stilbene



trans

$\lambda_{max} = 295$ nm

$\epsilon = 25000$



(cis)

↓

Steric crowding between ortho H-atoms

↓

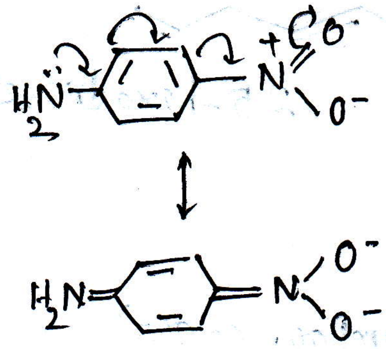
two phenyl rings are not coplanar

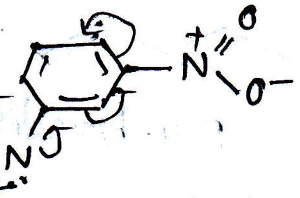
↓

283 nm ← lower λ_{max} ← less conjugation

$\epsilon = 12,300$

Problem} How to distinguish between m-nitroaniline and para nitroaniline?

λ_1 

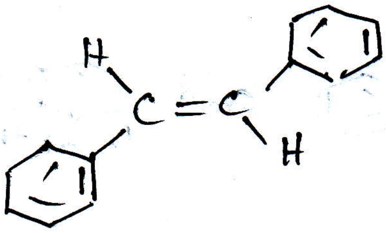
λ_2 

no extension of conjugation

conjugation increases

$\lambda_1 > \lambda_2$

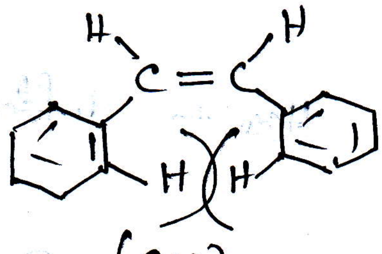
Problem} How to differentiate cis- and trans-stilbene



trans

$\lambda_{max} = 295$ nm

$\epsilon = 25000$



(cis)

↓

Steric crowding between ortho H-atoms

↓

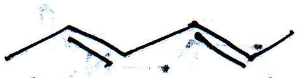
two phenyl rings are not coplanar

↓

less conjugation → lower λ_{max} ← 283 nm

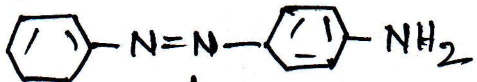
$\epsilon = 12{,}300$

Problem} How to differentiate between 2,4-hexadiene and 2,5-hexadiene



2,4-hexadiene

2,5-hexadiene

Problem i)  (yellow colour)

↓ on protonation

no colouration

(ii)  $\xrightarrow{^{-}OH}$ λ_{max} shifted to 235 nm !!

ethanolic soln

λ_{max} = 210 nm

(iii) How to differentiate  and  (napthalene)

(iv) (A, B) C_6H_8 $\xrightarrow{Br_2}$ (+) ve test

↓ Hydrogenation

C_6H_{12}

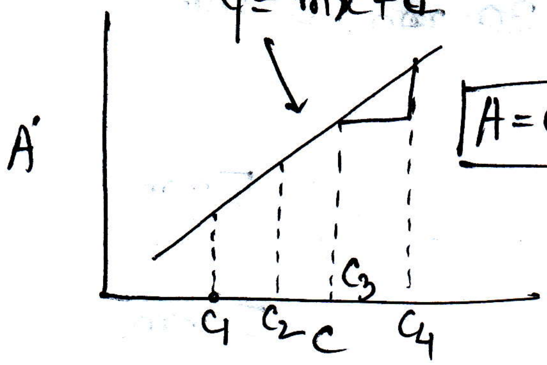
A ⟶ λ_{max} 256 nm

B ⟶ λ_{max} 200 nm

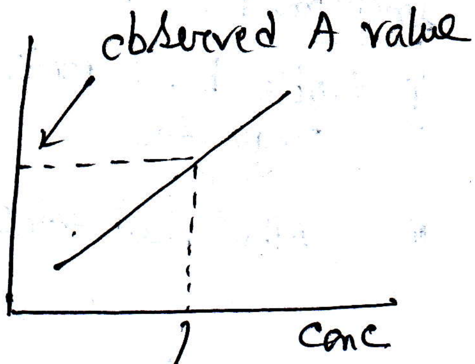
Importance of UV-VIS Spectroscopy :

1. Detection of conjugation and its nature
2. Study of extent of conjugation
3. Study of strain
4. Determination of geometrical configuration
5. Prediction of chemical change
6. Determination of concentration

$y = mx + d$



$\boxed{A = \epsilon . c . l}$



$\underbrace{C_1, C_2, C_3, C_4}$

Known concentration

↓

determine value = m

determine value of d

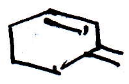
concentration can be calculated from A value

y = Knowns
m = Known
d = Known
x can be calculated ← Conc

How to predict λ_{max} value of conjugated diene

⇓

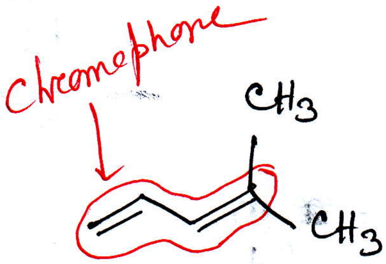
Woodward - Fieser ~~value~~ Rules (Emperical)

	Homo-annular	Hetero-annular
Base value	$\lambda = 253$ nm	214 nm
		

increments for

i) double bond extending conjugation	~~30~~ ~~nm~~ 30 nm
ii) Alkyl Substituent / ring residue	5 nm
iii) exocyclic double bond	5 nm

Example 1

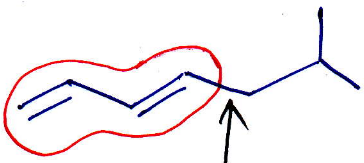


Base value = 214 nm (hetero annular)

2 x alkyl residue = 2x5
(CH_3 groups)

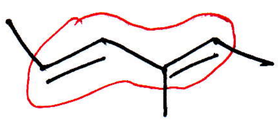
~~224~~ nm
224

λ_{obs} = 223 nm

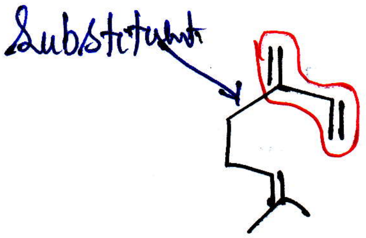


alkyl residue (1)

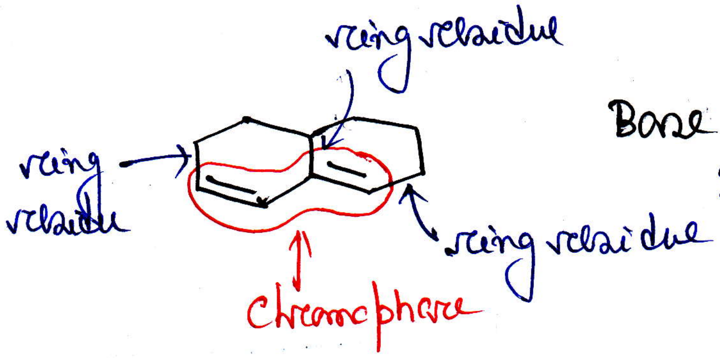
Base value = 214 nm
→ + 5 nm
219 nm



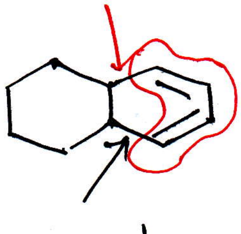
Base value = 214 nm
3 x alkyl residue = 3x5
229 nm



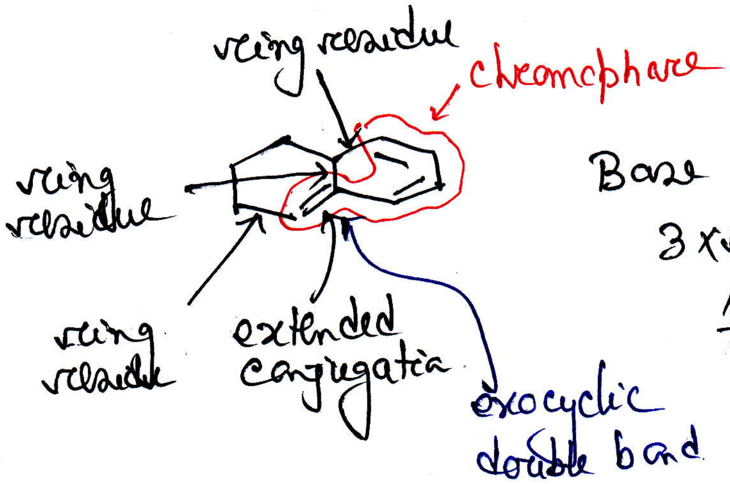
Base value = 214 nm
1x Subst = +5
219 nm



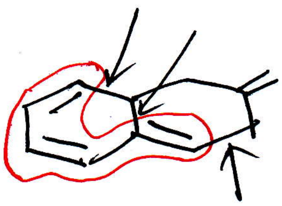
Base value => 214 nm
3 x ring residue = 3x5 nm
229 nm



Base value = 253 nm (Homo annular)
2 x ring residue = 2x5
263 nm



Base value = 253 nm
3 x ring residue = 2x5
1 x exocyclic double bond = 5
extended conjugation = 30
303 nm



Base value = 253 nm
extended conj. = +30
3 x ring residue = 3x5
Total = ?