Aim of the experiment

- Study the effect of solvent polarity and pH on the UV spectrum in term of λ max and absorption intensity and explain the results by electronic transition.

Experiment 5

Ultraviolet Spectroscopy - Effect of Solvent on λ_{max}

* Aim of the experiment * الهدف من التجربة

Study the effect of solvent polarity and pH on the UV spectrum in term of λ max and absorption intensity and explain the results by electronic transition.

⇐ دراسة التغير في الـ pH وفي الـ Solvent وتأثيرهم على λ_{max} أو تأثيرهم على absorption intensity.

* Absorption intensity = molar absorbity

⇐ من ثمّ نقوم بتفسير هذا التغير، كيف صار، وليصار؟

Chromophore

- The part of the molecule that responsible for imparting color to the to the molecule term chromophore.
- Chromophore is defined as any group which exhibits absorption of electromagnetic radiations in the visible or ultraviolet region.

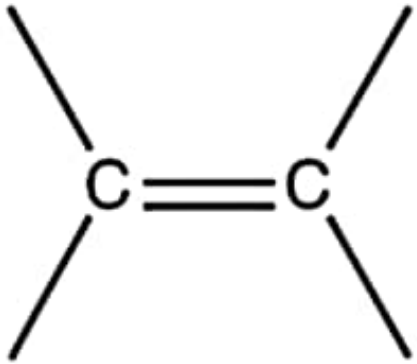
e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

date / /

(Chromophore)

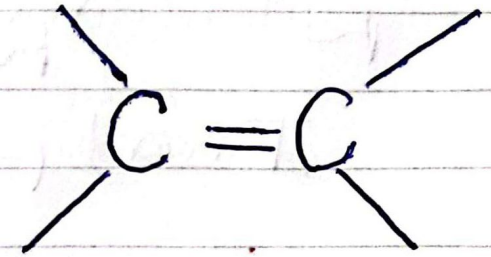
يعتبر جزء من الجزيئات مسؤولة عن إعطاء اللون المناسب، وبالإضافة إلى ذلك يعمل على إمتصاص الضوء في كل من الـ UV and Visibile.

- Chromophores in which the group is having **π** electrons undergo **π→π*** transitions.
- Ex: ethylens, acetylenes.



$\pi \longrightarrow \pi^*$

Example :- Ethylens, acetylenes



(Ethylens)

روابط π تتكون من π electrons هدفك بس تعرفوا electromagnetic radiations

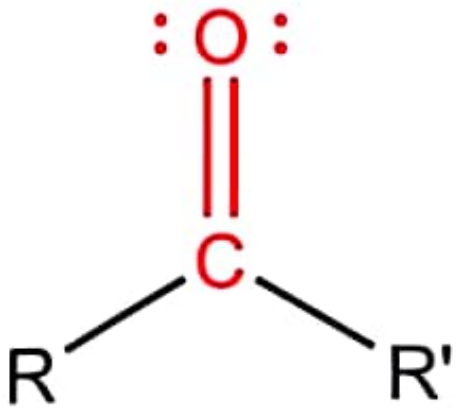
يصير لهم Transition من ال bonding Stage ال antibonding Stage

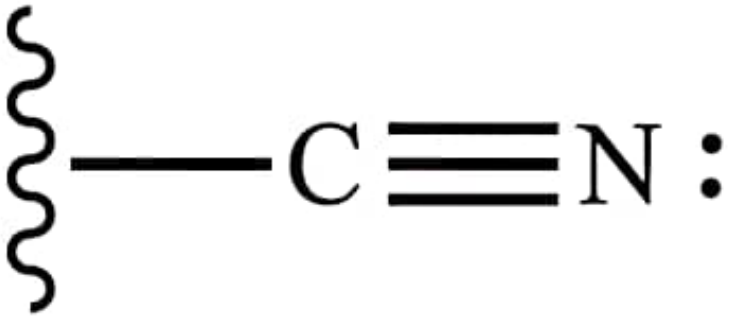
$\pi \longrightarrow \pi^*$ يعني

- Chromophores having both π electrons and n electrons undergo two types of transitions.

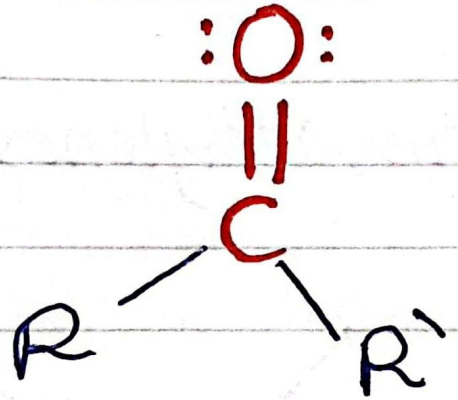
  π→ π* and n→ **π***

  Ex: carbonyl, nitrile.





$\pi \longrightarrow \pi^*$ and $n \longrightarrow \pi^*$



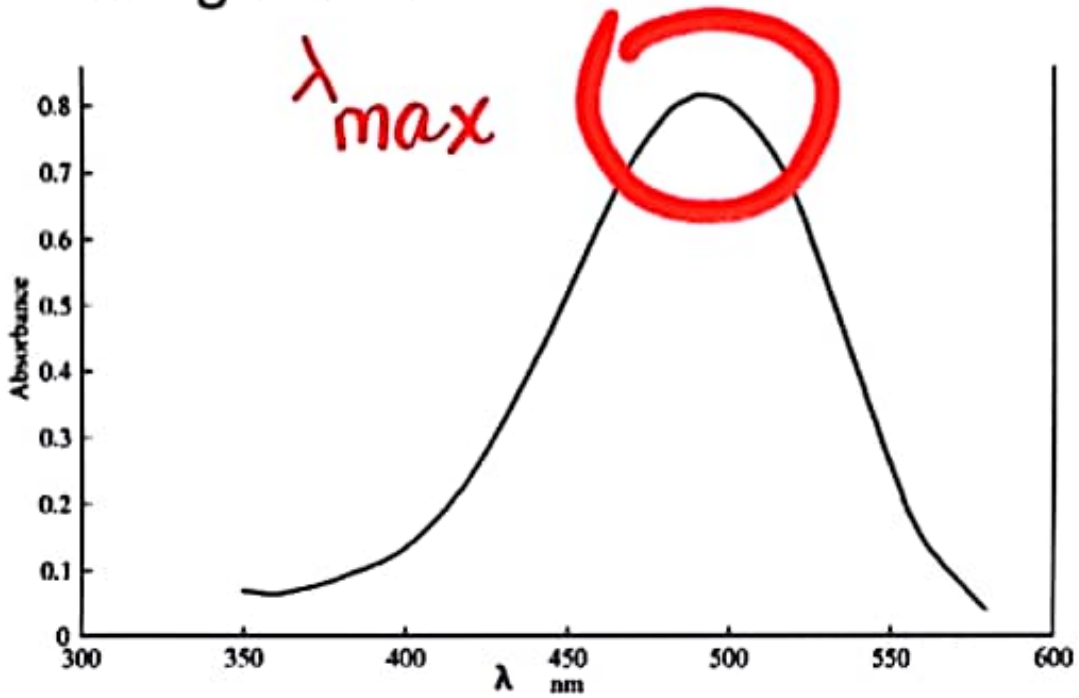
Carbonyl

* أقلّ تركيز تحتوي على ذلك ($=$) يعني π
* قانبًا عنها Lone pair

يصبح الإنتقال من $\pi \longrightarrow \pi^*$ أو $n \longrightarrow \pi^*$

Shifts and effect

- Position of the absorption maximum (λ max) and intensity of absorption can be modified in different ways by some structural changes or change of solvent



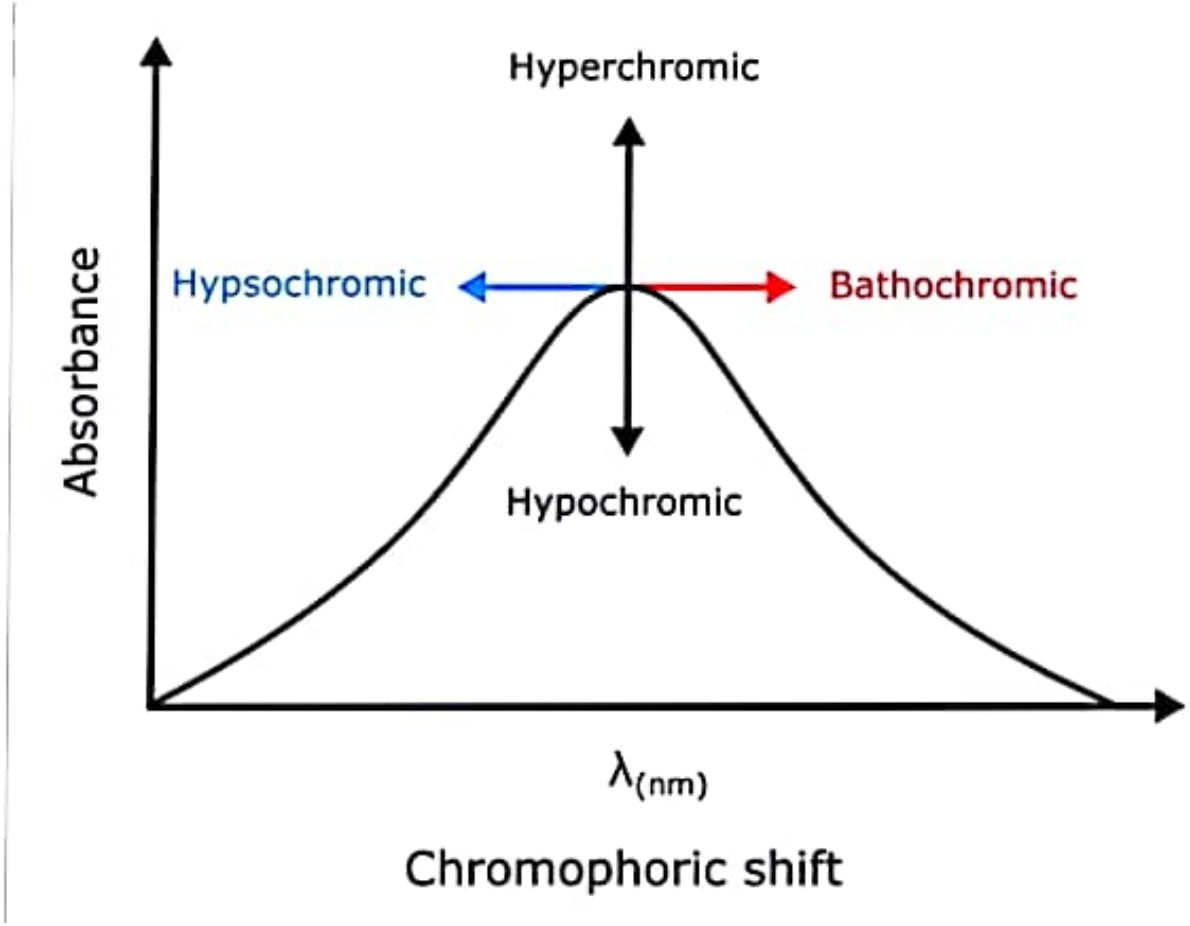
(Absorbance and λmax)

قيمة الـ absorbance (أعلى قيمة) تتأثر في كل من :

(1) Structural Changes → تغيّر المركّب تاعي

(2) Change of Solvent → تغيّر الـ Solvent للمركّب

Shifts and effect



a. Bathochromic Shift or Red shift

The shift of an absorption maximum towards longer wavelength or lower energy is called as bathochromic shift. The red color has a longer wavelength than the other colors in the visible spectrum, therefore this effect is also known as red shift.

b. Hypsochromic Shift or Blue Shift

The shift of an absorption maximum towards the shorter wavelength or higher energy is called hypsochromic shift. The blue color has a lower wavelength than the other colors in the visible spectrum and hence this effect is also known as blue shift.

c. Hyperchromic Effect

It is an effect that results in increased absorption intensity. The introduction of an auxochrome usually causes hyperchromic shift.

d. Hypochromic Effect

An effect that results in decreased absorption intensity is called hypochromic effect. This is caused by a group which distorts the geometry of the molecule

⇐ التغيّرات التي تحدث على λ_{max} هي ٤ تغيرات رئيسيّة مهمة الأحقية وهي الكاموديّة كما موضح بالورقة.

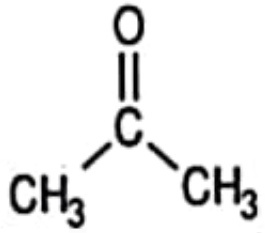
* Bathochromic Shift (Red Shift) : Longer wavelength
* Hypsochromic Shift (Blue shift) : Shorter wavelength

(التغيرات الخاصّة بالـ λ)

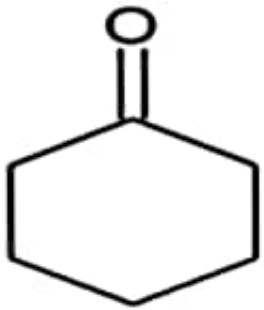
* Hyperchromic effect : Increase in the intensity of absorption
* Hypochromic effect : Decrease in the intensity " "

(التغير الخاص بالـ Absorption)

Structural change



e.g. Acetone which has λ_{max} = 279 nm

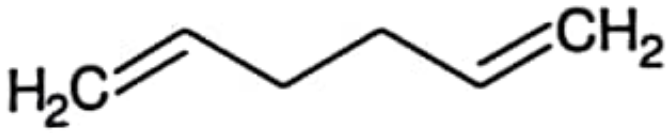


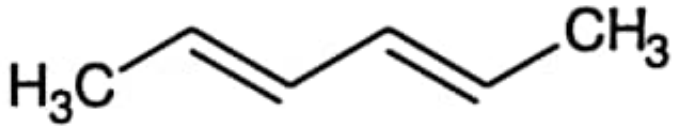
and that cyclohexane has λ_{max} = 291 nm.

When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

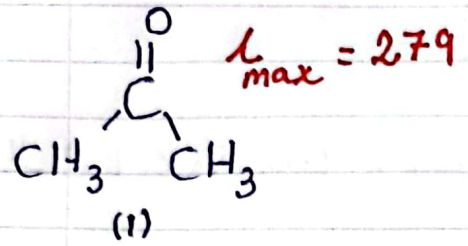
e.g. 1,5 - hexadiene has λ_{max} = 178 nm

2,4 - hexadiene has λ_{max} = 227 nm



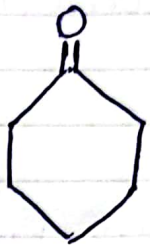


شرح الـ Structural Change



(1)

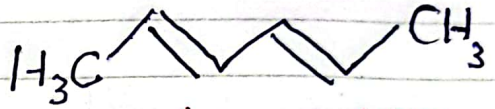
$\Rightarrow$



(2)

عندي مركبين نفس عدد الكربونات ونفس كل شيء ولكن المركّب رقم واحد شكله خطي (Linear) والثاني سايكل هون تضر عندي الستركشر واختلف عندي الطول الموجي حيث إنه السايكل أكبر من الـ Linear

$\lambda_{max} = 178$



$\lambda max = 227$

بالرغم عندي نفس المركبين بس في واحد Conjugated وواحد لأ !
وأكيد الـ Conjugated أكبر

شو تعني Conjugated ؟ $\Leftarrow$ Single – Duble – Single – D

ملحوظة أجا سؤال بالكويز كالتالي :-

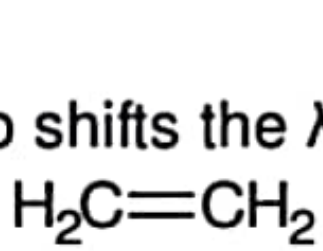
أي إله طول موجي أطول 1,4 dihexanol or 1,3 dihexanol ؟

1,3 dihexanol ليش ؟

لأنه Conjugated

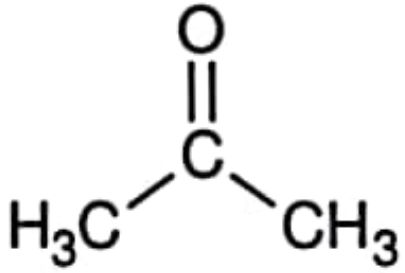
CHROMOPHORE

3. Conjugation of C=C and carbonyl group shifts the λ_{max} of both groups to longer wavelength.

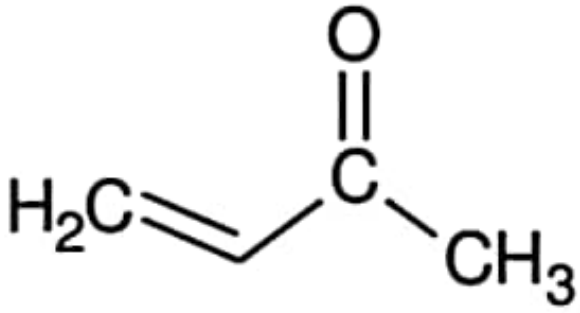


e.g. Ethylene has λ_{max} = 171 nm

Acetone has λ_{max} = 279 nm

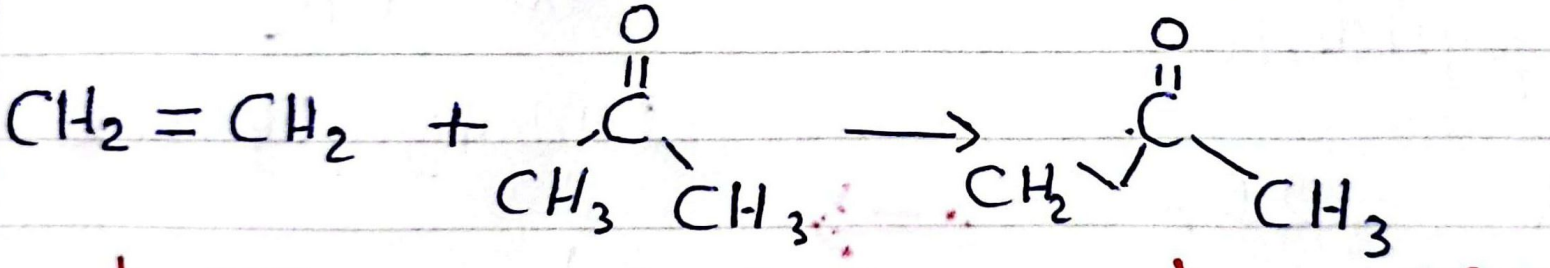


Crotonaldehyde has λ_{max} = 290 nm



Chromophore هي ال wavelength من الأشياء اللي تزيد ال

لحين بضيف أكثر من مركّب ما بعضها كمثال :-



(Auxochrome)

AUXOCHROME

The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light, altering the wavelength or intensity of absorption.

OR

The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

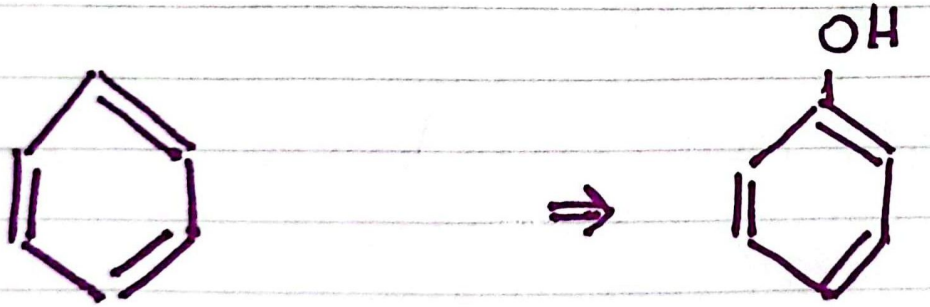
(Auxochrome)

عبارة عن Functional group بتضيف على الـ Chromophore

بيزيد من الإمتصاص والطول الموجي.

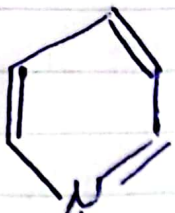
ميزتها هاي إنه تحتوي على non-bonding electrons وما بيرها إمتصاص عنطقة الـ UV أبدًا ولكن لما أضيفها على الـ Chromophore تغيّر الصفات تاعتها.

مثال :-



$\lambda_{max} = 255$

$\lambda_{max} = 270$



pyridine

$\lambda_{max} = 257$

$\varepsilon = 2750$

⟹ زيادة

2-methyl pyridine

$\lambda_{max} = 260$

$\varepsilon = 3560$

شو التغير يلي صار عندي بالإمتصاص والـ λ_{max} ؟

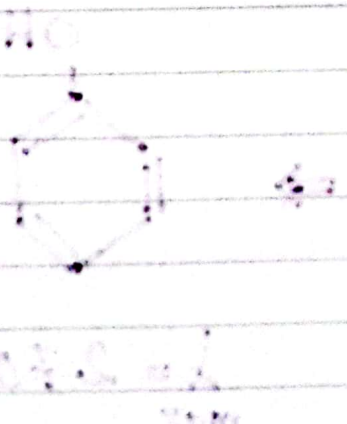
ضفنا ميثايل كروب (methly grap)

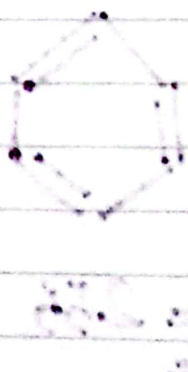
الذي يعتبر هو والهيدروكربون من الـ electron donating groups يعني ؟؟

يلي الكربون فيها مرتبط برابطة بسيطة مع الـ ring

يعني الكربونة إلكتروناتها مسحوبة لـ ring

الـ ring فيها الكترونات أكثر وهذا يؤدي إلى زيادة الإمتصاص والـ λ_{max}





ملحوظة مهمة :-

إضافة non-bonding مثل (OH, NH_2) يعمل على Shift λ_{max}

أمّا إضافة electron donating groub (CH_3-) يزيد من الإمتصاص

وتظل الـ λ عند نفسها .

Solvent change

- Solvents play an important role in UV spectroscopy.
- The common solvents used are water, methanol, ethanol, dilute acids and dilute alkalies.
- **The solvent** for a sample should be selected in such a manner that it **should neither absorb in the region of absorption nor affect the absorption of the sample**.
- The solvent exerts a profound influence on the quality and shape of spectrum
- The absorption spectrum of pharmaceutical substance depends practically upon the solvent that has been employed to solubilize the substance.
- A drug may absorb a maximum radiation energy at particular wavelength in one solvent but shall absorb partially at the same wavelength in another solvent.
- Eg. Bromophenol blue in HCL → λ_{max} at 437 nm
- Bromophenol blue in distilled water → λ_{max} at 591 nm

النقطة رقم (2) :- اختار أحد السولفنت الموجودات بالـلاب

النقطة رقم (3) :- طالازم يكون عندي Solvent ملوّن

النقطة رقم (4) :- ما يأثر الـSolvent على الخصائص مثل الـ λ و الامتصاص

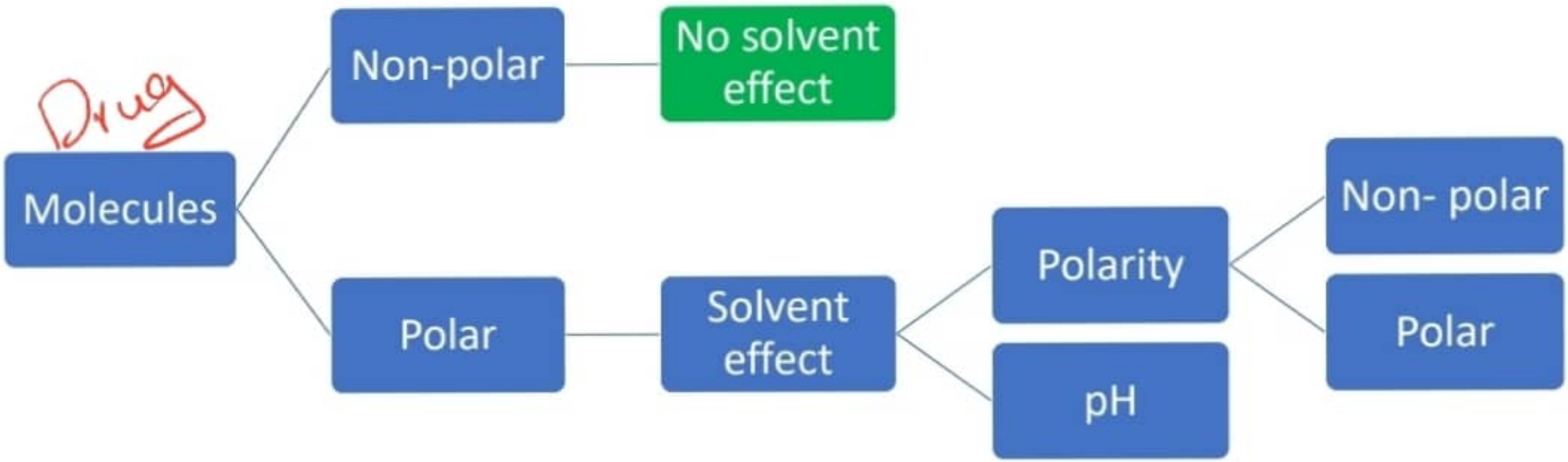
النقطة رقم (5) :- الـ drug لـ Solvent معيّن و λ_{max} معيّن، لو ضفت Solvent آخر ما راح يوصّل إلى λ_{max} وراح يصير عندي absorb partially

(تغيّرت عندي λ_{max} نتيجة تغير الـSolvent)

⇒ Bromophenol blue in HCl → λ_{max} = 437 (انتبهوا للأمثلة)

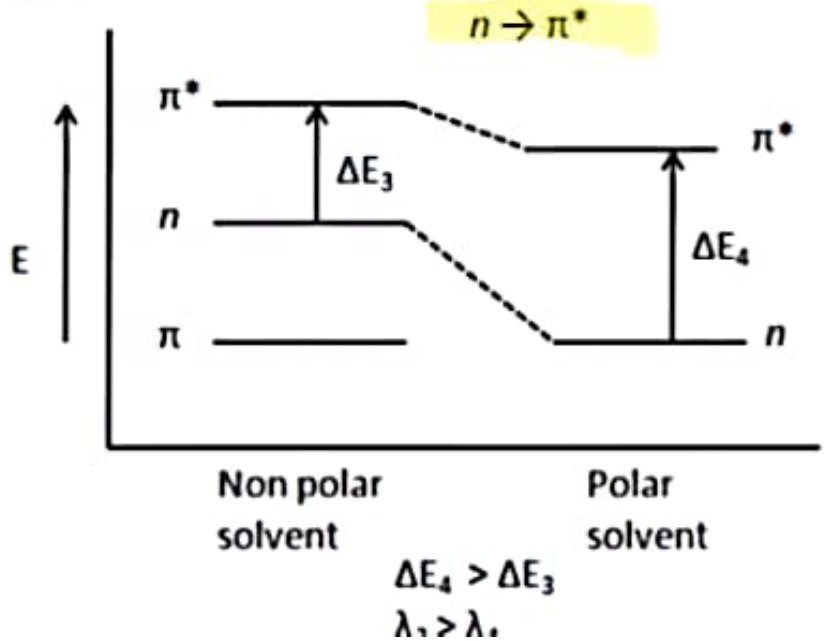
〃 〃 in water → λ max = 591

لاحظوا في الماء كانت أعلى من HCl


Drug
Molecules
Non-polar
No solvent effect
Polar
Solvent effect
Polarity
pH
Non- polar
Polar

Effect of the polarity of the solvent

- Polarity causes a pronounced effect on the position and intensity of absorption bands. This increase is due to the n-π* and π-π* transitions. In the presence of polar hydrolytic solvent (i.e. water) hydrogen bonds form with the lone pair of electrons of auxochrome. As a result, the auxochrome's energy lowers to an equal amount of the bond formation energy, and hence the energy gap between n and π* increases, so, a hypsochromic shift is observed for n-π* transition.



date / /

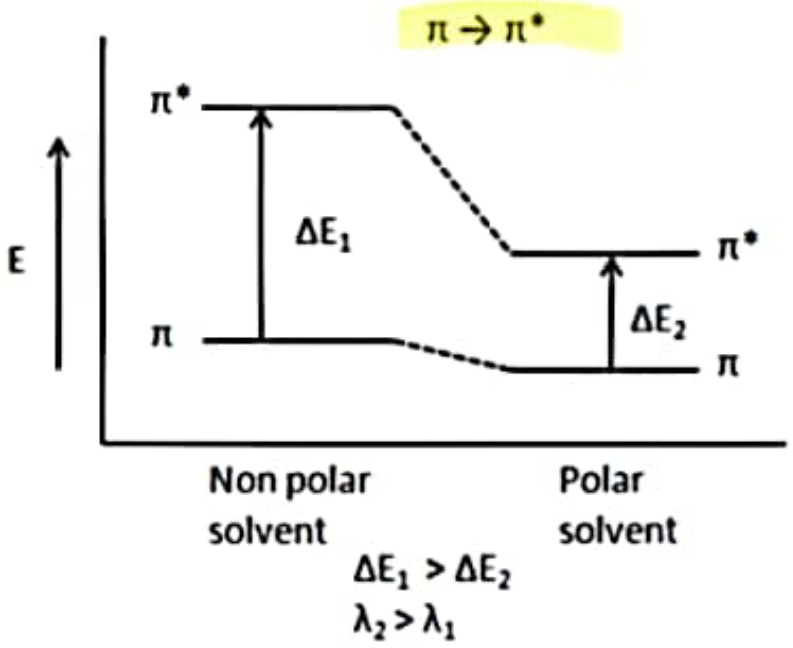
ال polarity واع تغيّر في position و intensity نتيجة تغيرات في
ال $\pi \rightarrow \pi^*$ و ال $n \rightarrow \pi^*$ ($n \rightarrow \pi^*$)

* لو استخدمت polar solvent مثل water، المركب تاعي أو drug تاعي
يحتوي على auxochrome (OH, NH_2 ..) هيدخل لقدرة إلها لقابلية
أنهم يعملوا H bond مع water (polar) فيصبح لديّ إنخفاض في
ال energe لدى ال n وبالتالي مقدار ال jump أكبر من $n \rightarrow \pi^*$ (كما موضح بالرسمة
علاقة عكسية في ال energe و ال λ)

($\pi \rightarrow \pi^*$)

* في polar واع يصير لل π^* أقل من أخطه في polar solvant يصير عندي
إنخفاض في π^* ويصبح لفرقه ΔE قليل بين π و π^*

- While for π-π^* transition the π^* orbital is more polar than π orbital therefore it is stabilized to a greater extent in the presence of a polar solvent. This will cause a bathochromic shift because the energy gap between π-π^* is reduced due to the stability of the π^* orbital.



Example :-

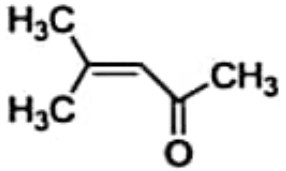


Table 4. Effect of solvent on the electronic transitions

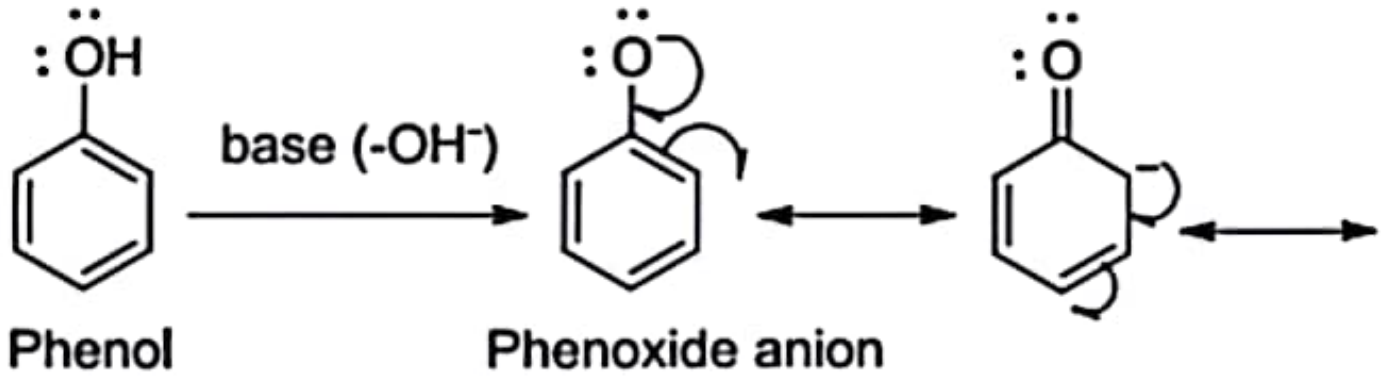
Solvent	$\pi \rightarrow \pi^*$		$n \rightarrow \pi^*$	
	λ	ε	λ	ε
Hexane	230	12,600	327	98
Ethanol	237	12,600	315	78
Water	245	10,000	305	60

الـ phenol وضعت في وسط قاعدي ($base.OH^-$) وتحوّل لـ Phenoxide anion

ويصير عندها negative Charge وتظل تتحرك هاي الـ negative داخل الـ ring وتلف.

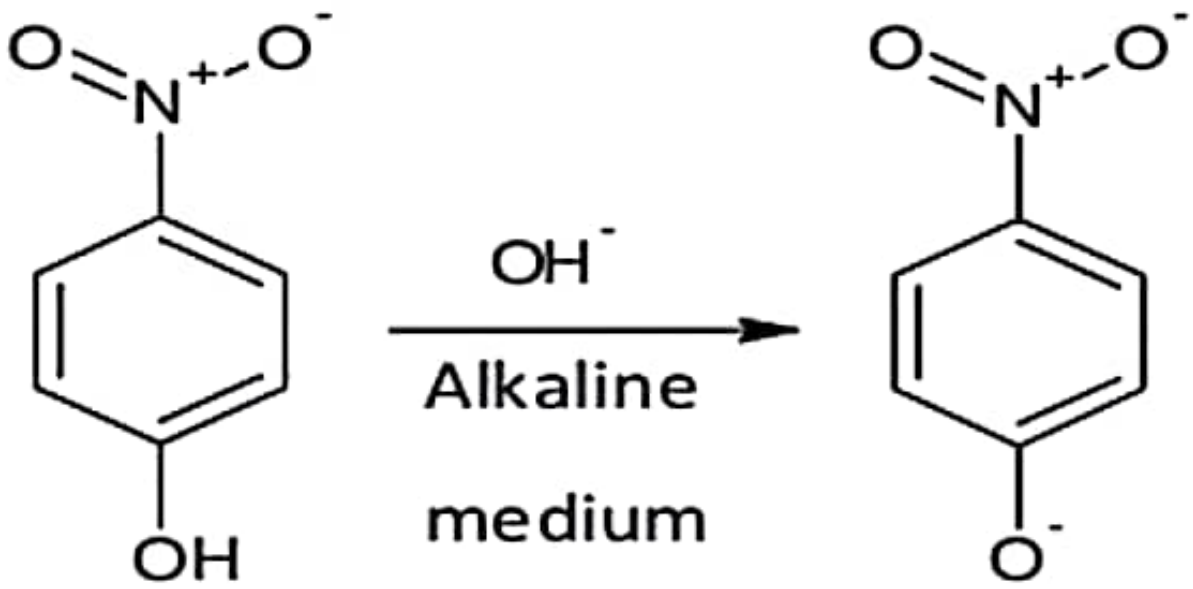
Effect of pH

- The pH of the sample solution can also have a significant effect on absorption spectra.
- The absorption spectra of certain aromatic compounds such as phenols and anilines change on changing the pH of the solution.
- Phenols and substituted phenols are acidic and display sudden changes in their absorptions maxima upon the addition of a base.
- After the removal of the phenolic proton, we get phenoxide ion. In the phenoxide ion lone pairs on the oxygen is delocalized over the π-system of the aromatic ring and increases the conjugation of the same.
- Extended conjugation leads to a decrease in the energy difference between π-π^* orbitals, which results in red or bathochromic shift (to longer wavelength), along with an increase in the intensity of the absorption.



	Neutral	Basic
λ_{max} =	210 (6200)	235 (9400)
	270 (1450)	287 (2600)

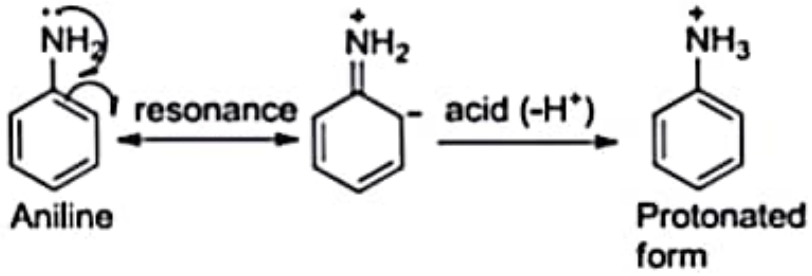
- In alkaline medium, p-nitrophenol shows red shift.



p-nitrophenol

λ_{max} = 255 nm λ_{max} = 265 nm

- Similarly, an aromatic amine gets protonated in an acidic medium which disturb the conjugation between the lone pair on nitrogen atom and the aromatic π-system. As a result, blue shift or hypsochromic shift (to shorter wavelength) is observed along with a decrease in intensity



Neutral	Acidic
λ_{max} = 230 (8600)	203 (7500)
280 (1430)	254 (169)

date / /

← شو بصير عندي لو مركّب يحتوي على amine group مش acid group

بحطها في acid med (وسط حمضي) يلي هو مركّب قاعدي (Aniline)

راح يزداد عندي عدد الهيدروجينات فصار عندي positive charge

وأصبحت الـ (–) على طرف الـ ring بعدما كانت lone pair فبعد ما حطيتها

في وسط حمضي تحولت من NH_2 إلى NH_3^+ بطّل عندي الـ lone pair حرّة

وإنهم ينتقلوا داخل الـ ring

⇒ قلّت حوسة الإلكترونات ← الـ Congeucated system ضعف — Lower wavelength

← راح تضعف الـ intensity

~ Hawazen Abdalah ... تـحـبـبـه ~