

# UV Spectra

Woodward and Fischer rule <sup>for</sup> diene <sup>de</sup> Triene Absorption:

Acyclic and heteroannular dienes	214 nm
Homoannular dienes	253 nm
-R (alkyl, including part of cyclohexic ring)	5 nm
-OR alkoxy	6 nm
-Cl, -Br	5 nm
-CH=CH - additional conjugation.	30 nm
EXOCYCLIC double bond	5 nm
-OCOR alkoxy	0 nm
$\begin{matrix} \beta & \alpha & \delta \\   &   &    \\ -C=C-C- \end{matrix}$ acyclic or 6-ring cyclic	215 nm
<del><math>\begin{matrix} \beta &amp; \alpha &amp; \delta \\   &amp;   &amp;    \\ -C=C-C- \end{matrix}</math></del> 5-ring cyclic	202 nm
aldehydes $-C=C-C-CHO$	210 nm
extended conjugation	30 nm
$\begin{matrix} \delta & \gamma & \beta & \alpha & \delta \\   &   &    &   & \\ -C=C-C=C-C- \end{matrix}$ etc homodiene component	39 nm

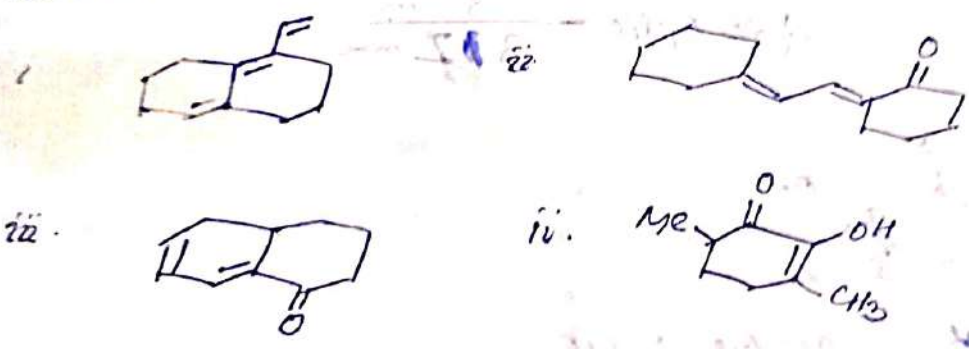
Increment (nm)	$\alpha$ ,	$\beta$	$\gamma$	$\delta$
-R (alkyl, including part of cyclohexic ring)	10 nm	12 nm	18 nm	18 nm
-OR alkoxy	35	30	17	31
-OH	35	30	30	50
-SR	-	80	-	-
-Cl	15	12	12	12
-Br	25	30	25	25
-OCOR	6	6	6	6
-NH <sub>2</sub> /NHR/-NR <sub>2</sub>	-	95	-	-
	-	5	-	-

UV

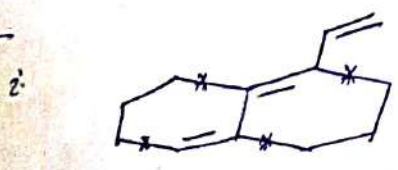
\*  $n \rightarrow \pi^*$  transition is more useful than  $\pi \rightarrow \pi^*$  transition for the detection of aldehydes and ketones.

Carbonyl ~~comp~~ groups show characteristic absorption due to non-bonding electrons on the oxygen atom. These non-bonding electrons are not tightly held, and hence  $\pi^*$  electrons and these are, therefore, excited to anti-bonding orbitals by lower energy UV radiation. Saturated aldehydes show three absorption bands, two of which are observed in the far ultraviolet region.  $\pi \rightarrow \pi^*$  transition absorbs strongly near 150 nm and  $n \rightarrow \pi^*$  transition absorbs near 190 nm. The third band ( $n \rightarrow \pi^*$ ) appears in near ultraviolet or the 270-300 nm region. The band ~~at~~ 200 nm due to either  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transition is very difficult to measure (since  $O_2$  of atmosphere absorbs in this region). So in the case of aldehyde or ketone  $n \rightarrow \pi^*$  transition is more useful than  $\pi \rightarrow \pi^*$  transition.

\* Calculate the  $\lambda_{max}$  for the following compounds:

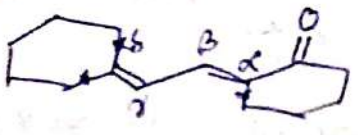


Ans



\* Base value  $\rightarrow 214 \text{ nm}$ .  
 Extended conjugation  $\rightarrow 30 \text{ nm}$   
 Ring residue  $\rightarrow 4 \times 5 = 20 \text{ nm}$ .  
 Exocyclic double bond  $\rightarrow 2 \times 5 = 10 \text{ nm}$   
 $\lambda_{max} = \overline{274 \text{ nm}}$

22.



215  
86  
301

Base value: 215 nm  
 extended conjugation  $\rightarrow$  30 nm  
 exocyclic double bond  $\rightarrow$  275 = 10 nm  
~~alpha~~  $\alpha$ -Substitution = 10 nm  
 $\zeta$ -Substitution = 1872 nm = 36 nm  


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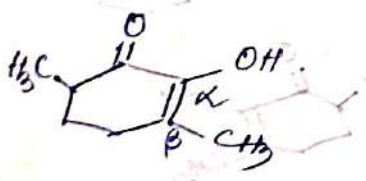
 $\lambda_{max} = 301 \text{ nm}$

iii.



Base value: 215 nm  
 extended conjugation: 30 nm  
 $\alpha$ -Substitution: 10 nm  
 $\zeta$ -Substitution: 18 nm  
 Homodiene component: 39 nm  
 Exocyclic:  $\frac{5 \text{ nm}}{307 \text{ nm}}$

iv.



Base value: 215 nm  
 $\alpha$ -OH group: 35 nm  
 $\beta$ -alkyl group: 12 nm  
 $\beta$ -Substitution: 12 nm  


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 274 nm

The maximum wavelength of absorption in the case of ...

\* 2,4,6-trimethylacetophenone shows UV absorption at 242 nm while p-methylacetophenone at 252 nm. Explain the observation.

Ans

Woodward rule give reliable results only for those compounds in which there is no strain around the chromophore. We know that in the case of extended conjugation, the position and absorption depends upon the length of the conjugated system. Longer the conjugated system higher will be the absorption maximum and longer will be the value of extinction coefficient. If in a structure, the  $\pi$  electron system is prevented from achieving coplanarity, there is a marked shift in the absorption maximum and extinction coefficient. Slight steric hindrance to coplanarity about a single bond has a very little effect on the position and intensity of the absorption maximum. If the steric hindrance to coplanarity about a single bond is more, there is a marked decrease in intensity and may accompany a red or blue shift. A blue shift is observed in case of 2,4,6-trimethylacetophenone which absorbs at 242 nm as compared to p-methylacetophenone at 252 nm. This is due to the fact - COCH<sub>3</sub> group is remain out of plane with benzene.

In the case of 2,4,6-trimethylacetophenone the presence of the three methyl groups in ortho position as a result conjugation decreases, so the  $\lambda_{max}$  decreases.

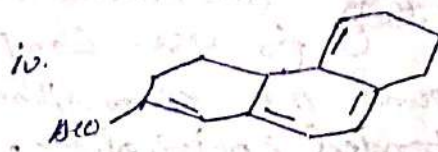
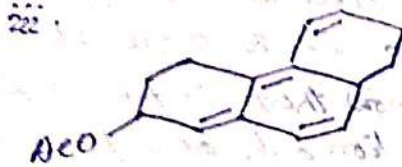
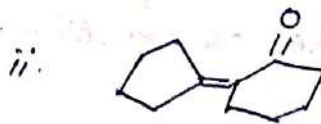
\* Increase in polarity of solvent shifts  $\pi-\pi^*$  band to longer wavelength but  $n-\pi^*$  band to shorter wave length.

Ans

The transitions of polar bonds, like C=O but not ethylene, are affected by solvent polarity. As solvent polarity is increased,  $\pi-\pi^*$  bands undergo red shifts. This is so since excited state is more polar than the ground state is more polar than the ground state and hence stabilization is greater relative to the ground state in polar solvents. The  $n-\pi^*$  bands undergo blue shifts, since ground state with two  $n$  electrons receives greater stabilization than the excited state with only one  $n$  electron. These opposite trends are clear by examining the data of mesityl oxide.

Solvent	$\pi-\pi^*$	$n-\pi^*$
n-hexane	230 nm	327 nm
Water	245 nm	355 nm

\* Calculate  $\lambda_{max}$  of the following compounds:



Ans



Base value: 215 nm

Extended conjugation: 30 nm

$\alpha$ -cyclic double bond: 5 nm

$\beta$ -residue: 12 nm

$\delta$ -residue: 18 nm

280 nm



Base Value: 215 nm

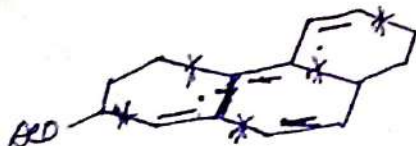
$\alpha$ -cyclic double bond:  $2 \times 10$  nm

$\alpha$ -residue = 10 nm

$\beta$ -residue = 12 nm

259 nm

\*



Heteroannular diene = 214 nm

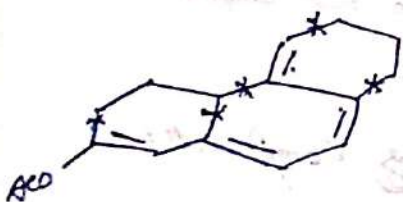
Extended conjugation = 30 nm

Ring residue =  $5 \times 5 = 25$  nm

Exocyclic double bond =  $3 \times 5 = 15$  nm

$$\lambda_{max} = \underline{284 \text{ nm}}$$

\*



Lactid  $\rightarrow$  253 nm

Extended conjugation =  $2 \times 30 = 60$  nm

Ring residue =  $5 \times 5 = 25$  nm

Exocyclic double bond =  $3 \times 5 = 15$  nm

$\text{CH}_3\text{COO} - = 0$

$$\underline{353 \text{ nm}}$$

\* Define the following terms with suitable example:

i. Auxochrome

ii. Bathochromic shift

Auxochrome:

The attachment of substituent groups in place of hydrogen on a basic chromophore structure changes the position and intensity of an absorption band of the chromophore. The substituent group may not give rise to the absorption of the ultraviolet radiation themselves, but their presence modifies the absorption of the principal chromophore.

Substituents that increase the intensity of the absorption, and possibly the wavelength are called auxochromes.

Typical auxochromes include methyl, hydroxyl, alkoxy, halogen and amino groups.

# Bathochromic Shift:

Bathochromic shift is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength (lower frequency). Because the red colour in the visible spectrum has a longer wavelength than most other colours, the effect is also commonly called a red shift.

For example as solvent polarity is increased,  $\pi-\pi^*$  bands undergo red shifts.

\* Calculate  $\lambda_{max}$  of the following compounds:



Ans



Base value - 214 nm

Extended conjugation - 30 nm

Ring residue  $\rightarrow 5 \times 5 = 25$  nm

Exocyclic double bond  $\rightarrow 5 \times 3 = 15$  nm

$$\lambda_{max} = \underline{284 \text{ nm}}$$



Base value: 215 nm

Ring residue:  $2 \times 12 = 24$  nm

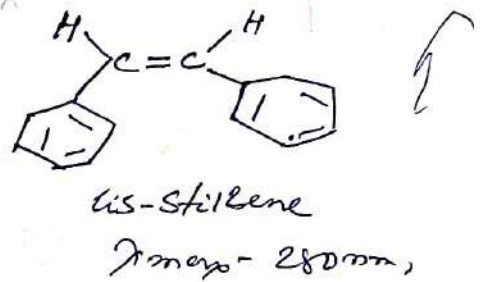
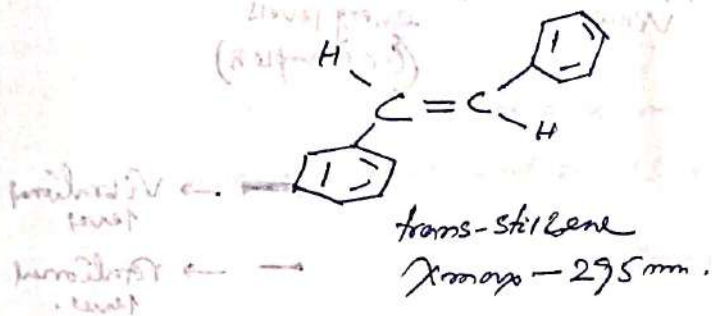
Exocyclic double bond = 5

$$\lambda_{max} = \underline{244 \text{ nm}}$$

\* cis- and trans- isomer of stilbene absorbs  $\lambda_{max}$  at 283 nm and 295 nm respectively in EtOH - Explain

Ans

In compounds where geometrical isomerism is possible e.g. in stilbene the E-isomer absorbs at a longer wave length with greater intensity than Z-isomer due to steric effect. Coplanarity is needed for the most effective overlap of the  $\pi$ -orbitals and increased ease of the  $\pi \rightarrow \pi^*$  transition. As trans-isomer achieved coplanarity  $\pi \rightarrow \pi^*$  transition occurs easily at higher wave length (lower energy transition). The Z-isomer is forced into a nonplanar conformation due to steric effect. As a result effective overlap of the  $\pi$ -orbitals not occur and transition take place at lower wave length (high energy transition)



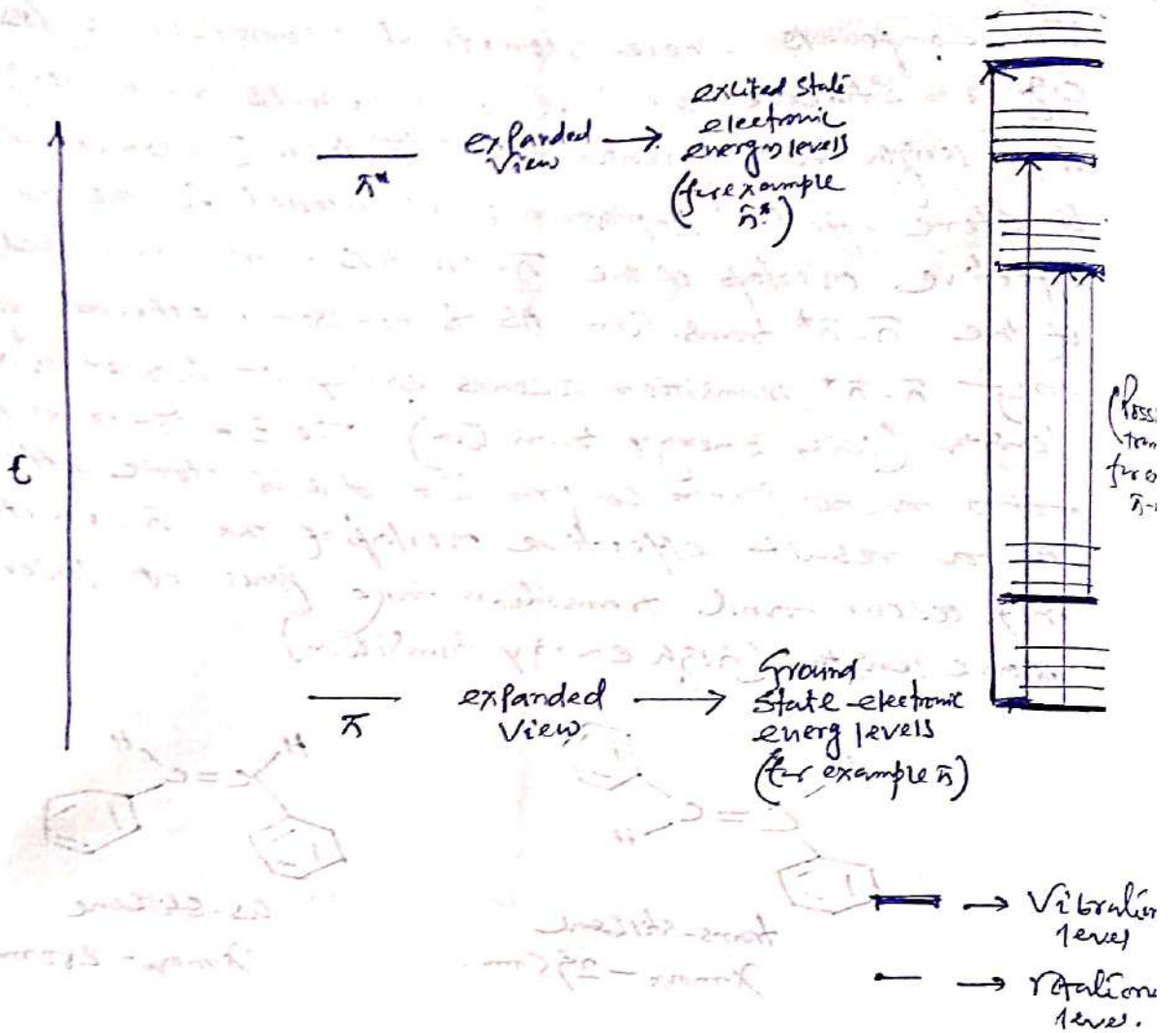
\* UV Spectroscopy shows a broad hump rather than sharp peak - Explain.

Ans

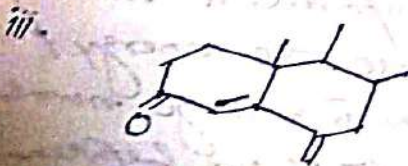
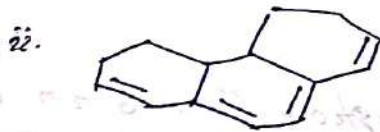
Absorption bands in an ultraviolet spectrum are typically very broad when compared to an infrared or NMR spectrum. This is because, the energy put into the sample is sufficient to allow a large number of different electronic transition to occur between the several different allowed vibrational and rotational energy levels of the molecule. No doubt, each transition is quantized, however, the  $\Delta E$  values are very close, so that complete resolution in the resolution phase is not possible. Thus a broad band is displayed which consists of all these overlapped transitions.



In other words, if only transitions in electron energy levels were involved the UV/vis spectra for all compounds would consist of fairly sharp lines, i.e. very narrow absorption bands.

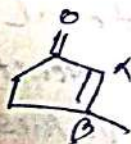


\* Calculate  $\lambda_{max}$  of the following compounds:



Ans

i.



In MeOH solvent correction is not required

Base value: 202 nm.

~~Ring residue: 2 x 5 = 10 nm~~

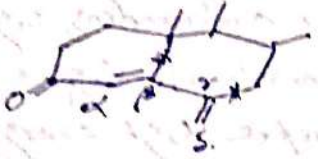
Substitution at  $\beta$ -position: 12 x 2 = 24 nm

~~202 + 10 + 24 = 226 nm~~



Basic: 258 nm  
 Extended conjugation:  $2 \times 30 = 60$  nm  
 Ring residue:  $4 \times 5 = 20$  nm  
 exocyclic double bond:  $2 \times 5 = 10$  nm  

$$\lambda_{max} = \underline{348 \text{ nm}}$$



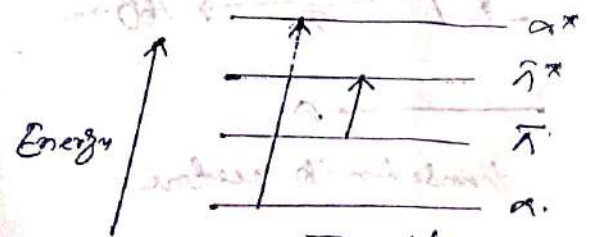
Base value: 215 nm  
 Extended conjugation = 30 nm  
 $\beta$ -Substitution = 12 nm  
 $\gamma$ -Substitution = 18 nm  
 exocyclic double bond =  $2 \times 5 = 10$  nm  

$$\lambda_{max} = \underline{285 \text{ nm}}$$

\* Ethylene displays two  $\lambda_{max}$  value in its UV-absorption spectrum. Explain.

Ans

Ethylene displays two ~~transition~~  $\lambda_{max}$  value in its UV absorption spectrum due to  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  transition. Sigma bonds are in general, very strong, this therefore is a high energy process and very short wave length i.e. high energy Ultraviolet light  $\approx 150$  nm is required. On the other hand  $\pi \rightarrow \pi^*$  transition required lesser energy than  $\sigma \rightarrow \sigma^*$  transition and occur at higher wave length compared to  $\pi \rightarrow \pi^*$  transition (170-190 nm).



Transition of ethylene molecule.

\* Indicate the type of electronic transition

Compound	Waves
i. Cyclopropane	170 nm
ii. CH <sub>3</sub> COCH <sub>3</sub>	166, 187, 279 nm
iii. Mesityl oxide	230, 317 nm

Justify your answer.

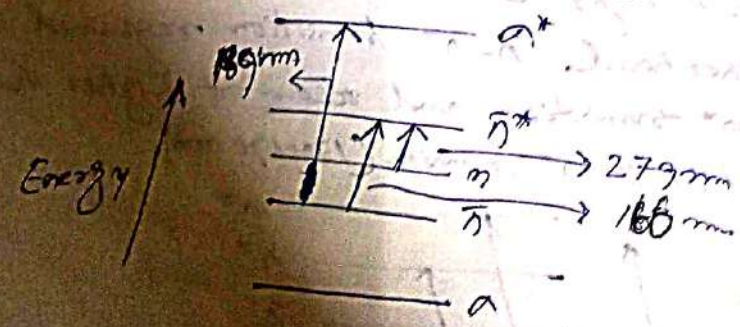
i. Cyclopropane: A transition of  $\sigma$  electron from a bonding sigma orbital to the higher energy antibonding sigma orbital occurs in this case ( $\sigma \rightarrow \sigma^*$  transition). Sigma bonds are, in general very strong, this therefore high energy  $\sigma$  and require very short wave length.

Cyclopropane	Transition type	Wavelength
	$\sigma \rightarrow \sigma^*$	170 nm

Wavelength for  $\sigma \rightarrow \sigma^*$  transition is somewhat longer than normal ~~is~~ alkane due to greater reactivity and lesser strength ~~than normal alkane~~.

ii. CH3COCH3: Acetone shows three transitions at 166, 187 and 279 nm due to  $n \rightarrow \sigma^*$ ,  $n \rightarrow n^*$  and  $\pi \rightarrow n^*$  transitions.

In  $n \rightarrow n^*$  transition an electron of unshared electron on oxygen is excited to  $n^*$  antibonding orbital. This transition involve least amount of energy compared to  $n \rightarrow \sigma^*$  and  $\pi \rightarrow n^*$  transition and therefore, the transition give rise to an absorption band at longer wavelength.

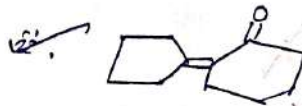
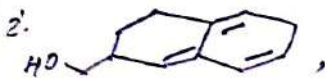


Transition in acetone.

iii Mesityl oxide :

In mesityl oxide transition at 230nm and 329nm are due to  $\pi-\pi^*$  and  $n-\pi^*$  transition. Due to conjugation the wavelength for  $\pi-\pi^*$  and  $n-\pi^*$  transition is somewhat larger than normal this type of transition.

\* Calculate  $\lambda_{max}$  of the following compounds:



Base value  $\rightarrow 214 \text{ nm}$

Ring residue  $\rightarrow 4 \times 5 = 20 \text{ nm}$

Exocyclic double bond  $= 2 \times 5 = 10 \text{ nm}$

$\lambda_{max} = 244 \text{ nm}$

\* The  $n-\pi^*$  transition of acetone occurs at higher wavelength than that of  $\pi-\pi^*$  transition but absorption band due to  $n-\pi^*$  transition has less intensity. - Explain

Ans:

In the case of  $n-\pi^*$  transition, an electron of unshared electron pair on a hetero atom (here oxygen) is excited to  $\pi^*$  antibonding orbital. The transition involves least amount of energy than  $\pi-\pi^*$  transition and therefore, this transition give rise to an absorption band at higher wavelengths. This  $n-\pi^*$  transition is forbidden by symmetry consideration, thus the intensity of the band due to this transition is low, although the wavelength is ~~low~~ long.

\* Calculate the  $\lambda_{max}$  of the following compound

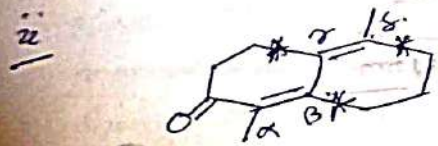


Transoid — 214 nm

Extended conjugation — 30 nm

Ring residue —  $4 \times 5 = 20$  nm

Exocyclic double bond = 10 nm  
 $\lambda_{max} \rightarrow 274$  nm



Base value  $\rightarrow 215$  nm

Extended conjugation  $\rightarrow 30$  nm

Exocyclic double bond  $\rightarrow 2 \times 5 = 10$  nm

$\alpha$ -Substitution  $\rightarrow 10$  nm

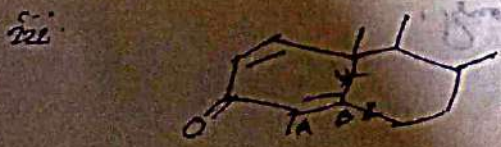
$\beta$ -Substitution  $\rightarrow 12$  nm

$\gamma$  - "  $\rightarrow 18$  nm

$\delta$  - "  $\rightarrow 2 \times 18 = 36$  nm

$\lambda_{max} \rightarrow 331$  nm

215  
 116  
 ---  
 331



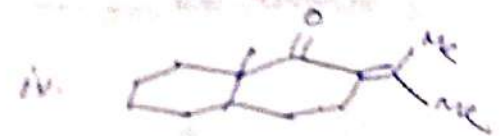
Base value  $\rightarrow 215$  nm

$\alpha$ -Substitution  $\rightarrow 10$  nm

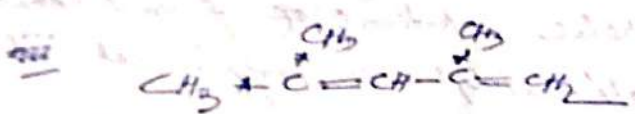
$\beta$ -Substitution  $\rightarrow 2 \times 12 = 24$  nm

Exocyclic double bond  $\rightarrow 5$  nm

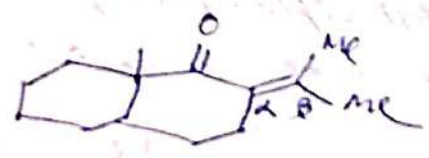
Calculate  $\lambda_{max}$



Base value  $\rightarrow 214 \text{ nm}$   
 extended conjugation  $\rightarrow +30 \text{ nm}$   
 $\alpha$ -cyclic double bond  $\rightarrow 3 \times 5 \text{ nm} = 15 \text{ nm}$   
 long residue  $\rightarrow 5 \times 5 \text{ nm} = 25 \text{ nm}$   
 $\lambda_{max} = 284 \text{ nm}$



Base value  $\rightarrow 214 \text{ nm}$   
 Alkyl substitution  $\rightarrow 3 \times 5 = 15 \text{ nm}$   
 $\lambda_{max} = 229 \text{ nm}$

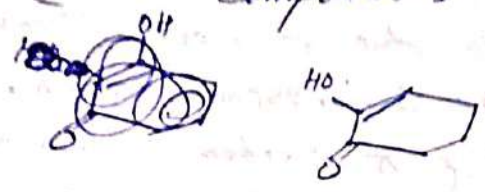


Base value  $\rightarrow 215$   
 $\alpha$ -cyclic  $\rightarrow 5 \text{ nm}$   
 $\alpha$ -substitution  $\rightarrow 10 \text{ nm}$   
 $\beta$ -substitution  $\rightarrow 2 \times 12 = 24 \text{ nm}$   
 $\lambda_{max} = 254 \text{ nm}$

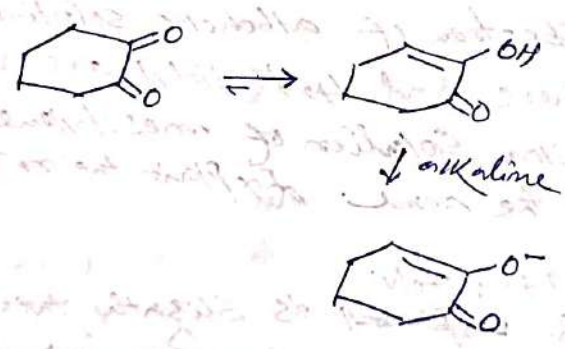
\* Calculate the energy of radiation in  $\text{kJ/mol}$ , the wavelength of which is  $12\text{A}$ ,  $c = 3 \times 10^8 \text{ m/s}$  and  $h = 6.624 \times 10^{-34} \text{ J/s}$

Ans do yourself

\* A bathochromic shift is observed by the addition of trace amount of alkali to compound-1. Explain



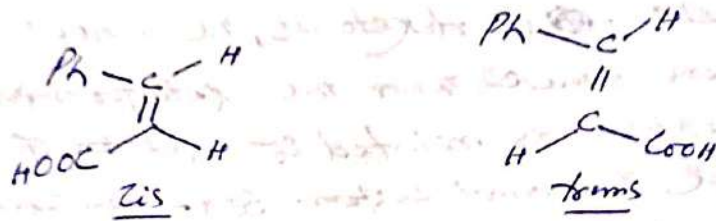
Ans In cyclic  $\alpha$ -diketones, the enolic form is generally more stable than the keto form and therefore, absorption is related to that of an  $\alpha, \beta$ -unsaturated carbonyl system. Six-membered cyclic  $\alpha$ -diketone known generally as diosphenols, exist in solution largely in the enolised form. In alkaline solution the absorption shifts to about  $50\text{nm}$  to longer waves, due to the formation of enolate ion to enable diosphenol structures to be characterized.



\* Trans-cinnamic acid absorbs at higher wavelength compared to cis cinnamic acid.

Ans.

If the compound containing alkene chromophore is capable of existing as geometrical isomers, the trans-isomer is found to absorb at longer wavelength with higher value of extinction coefficient as compared to cis-isomer. It is due to more effective  $\pi$  orbital overlap possible in the trans-isomer, which, thus, achieves coplanarity of  $\pi$  electron system more readily. Cinnamic acid exists in two isomers:



Due to greater crowding in cis-form (both bulky groups are on the same side), the geometry of the alkene chromophore is distorted and departure from coplanarity results. Thus  $\pi \rightarrow \pi^*$  transition in cis-cinnamic acid takes place at lower wave length with lower extinction coefficient.

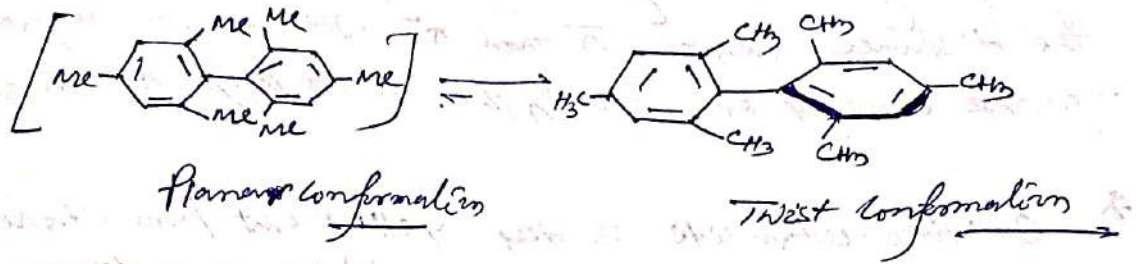
\* The UV spectra of alcoholic solution of equal concentration of toluene and 4,4'-bitolyl are very much different, however similar solution of mesitylene and 2,3,6-trimethylbenzene are almost the same. Explain the result.

Ans

4,4'-bitolyl is slightly twisted, the angle of twist is small, therefore, conjugation between the rings is not affected. 4,4'-bitolyl thus shows a very intense absorption band and its spectrum is completely different from toluene where conjugation is only due to one benzene ring. Biphenyl derivatives with bulky substituents in the ortho position like in 2,6-mesitylene are most stable in twisted conformation than in planar conformation, which suffers serious nonbonded repulsions from the juxtaposed substituents.

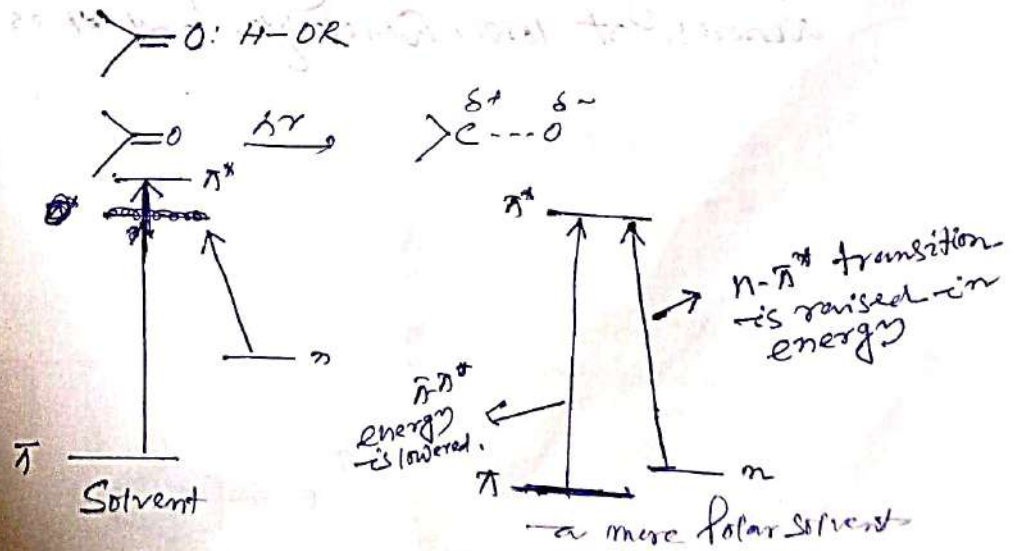


The loss of conjugation in the twist conformation of *trans*-1,2-dimethylcyclohexa-1,4-diene is reflected in its UV spectral data, which is now structurally is like two moles of mesitylene:



\* Acetone absorbs at 279 nm in *n*-hexane while in water the  $\lambda_{max}$  is at 264.5 nm. Explain

Ans One can explain this blue shift on the basis of hydrogen bonding. When the nonbonded electrons on the oxygen coordinate with a hydroxylic solvent, the net energy of the  $\pi$  electrons is lowered. Thus the distance to the  $\pi^*$  level will be higher and as a result in a polar solvent the  $n \rightarrow \pi^*$  transition will be of higher energy or lower wave length (blue shift).



Solvent effect on  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transition.

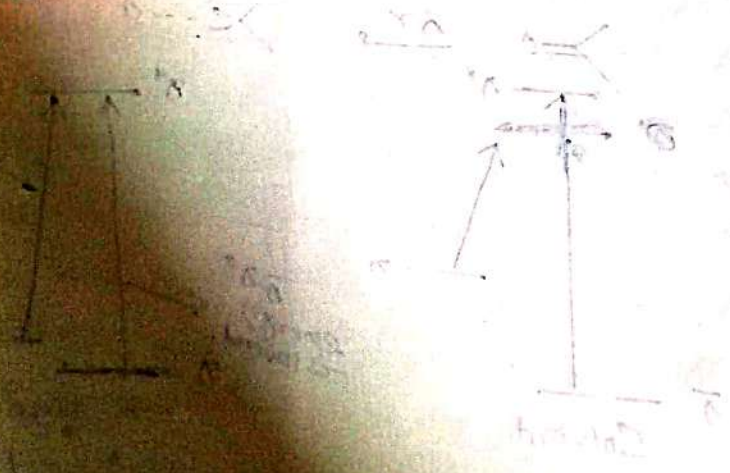
The  $\pi-\pi^*$  transition, on the other hand shifts to longer wavelength (lower energy) in a more polar solvent. The polar excited state of the  $\pi-\pi^*$  transition is stabilized by hydrogen bonding in more polar solvent. This lowers the distance between  $\pi$  and  $\pi^*$  with a subsequent lowering in the energy or raising the wavelength of transition.

\* O-Nitroacetamide is deep yellow but para-nitroacetamide is yellow. Why is the colour of 'o'-isomer is deeper?

The ortho isomer exhibits intramolecular hydrogen bonding whereas the para isomer shows intermolecular hydrogen bonding. Intermolecular or intramolecular hydrogen bonding stabilises the excited state of a molecule to the greater extent than the intermolecular hydrogen bond. Clearly, the electronic excitation energy required for o-isomer is smaller and thus, absorption occurs at longer wavelength and result in deepening of the colour.

\* Benzene is colourless but its isomer, fulvene is yellow. How will you explain it?

Ans. Fulvene is an isomer of benzene ( $C_6H_6$ ). Resonance stabilises the ground state of benzene compared to its excited state whereas fulvene is stabilised in the excited state. Thus the electronic excitation energy required for fulvene is lower than that for benzene. As a result of this, fulvene absorbs at higher wavelength which makes it yellow in colour. Benzene absorbs at lower wavelength and it is colourless.



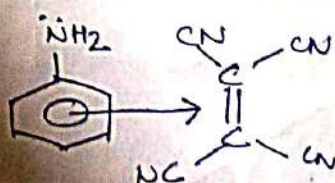
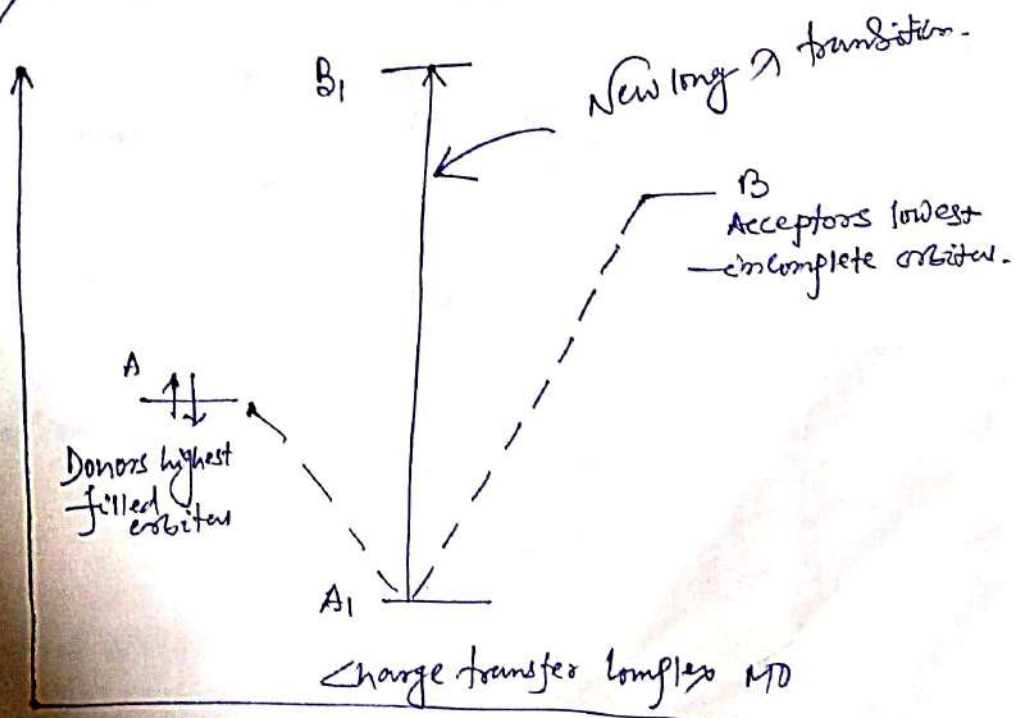
When two colorless liquids aniline and tetracyanoethylene are mixed, a deep blue colour develops - Explain.

Ans:

When aniline is dissolved in chloroform and tetracyanoethylene (acceptor) is added to it, a deep blue solution results. These colour shifts are due to the formation of complexes between the pair of molecules. As a result, two new molecular orbitals are formed which undergo new electronic transition.

The formation of these complexes involves the transfer of electronic charge from an electron rich molecule to an electron deficient molecule with molecular orbitals of suitable energy and symmetry. These complexes are called charge transfer complexes.

The filled  $\pi$ -orbital (A) in the donor molecule overlaps with depleted orbitals (B) in the acceptor molecule. Due to this, two new molecular orbitals are formed. These are (i) the low energy molecular orbital (occupied) in the ground state ( $A_1$ ) ii. the upper molecular orbital ( $B_1$ ). The transitions from  $A_1$  to  $B_1$  results in the formation of new absorption bands.



Aniline - tetracyanoethylene complex