

UNIT 12

IDENTIFICATION OF COMPOUNDS USING UV SPECTROSCOPY

Structure

12.1	Introduction	$\pi - \pi^*$ Transitions
	Expected Learning Outcomes	$n - \pi^*$ Transitions
12.2	Applications of Electronic Spectroscopy and Woodward Rules for Calculating λ_{max} of - Conjugated Dienes	12.4 Representative Problems
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12.3	Solvent Effects on Electronic Structure	12.6 Terminal Questions
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12.1 INTRODUCTION

In the previous unit, you have learnt about an introduction to UV-visible spectroscopy along with the basics of electromagnetic radiation. Also you have learnt about some important terms used in this context. In this unit, you will actually learn how to identify small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy. The rules to predict the position of absorption maxima in conjugated dienes and enones will then be presented. The unit will conclude with a discussion of effect of solvents on $n - \pi^*$ and $\pi - \pi^*$ transitions in carbonyl and unsaturated compounds and some representative problems based on these.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ understand the applications of Electronic Spectroscopy and Woodward rules to predict the absorption maximum for α, β -unsaturated compounds;

- ❖ explain the effect of solvent on $n - \pi^*$ and $\pi - \pi^*$ transitions in electronic spectra; and
- ❖ be able to solve problems on UV-vis spectroscopy for small organic molecules.

12.2 APPLICATION OF ELECTRONIC SPECTROSCOPY AND WOODWARD RULES FOR CALCULATING λ_{\max} OF α, β - CONJUGATED DIENES

In the previous unit, you have learnt about the term chromophore. In this section, we shall discuss the applications of electronic absorptions of only two of the more important chromophores in more detail. These are the ethylenic and the carbonyl chromophores. We will also look into the Woodward rules for calculating λ_{\max} of conjugated dienes. In addition, we shall have a brief look at the absorptions of the acetylenic and the benzenoid chromophores.

12.2.1 Ethylenic Chromophore

As you know ethylene has five σ bonds (four C–H and one C–C) and one π bond. If we denote σ molecular orbitals as σ_1, σ_2 etc., and consider only the twelve valence electrons, the ground state electronic configuration of ethylene is $(\sigma_1)^2(\sigma_2^*)^2(\sigma_3)^2(\sigma_4^*)^2(\sigma_5)^2(\pi)^2$. If we consider only the highest σ orbital, the ordering of the molecular orbitals is as shown in Fig. 12.1.

In ethylene only four electronic transitions are possible which are $\pi - \pi^*$, $\sigma - \sigma^*$, $\pi - \sigma^*$ and $\sigma - \pi^*$. Out of these the latter two are symmetry forbidden. Of the other two, you can see from the Fig. 12.1, the $\pi - \pi^*$ transition requires less energy. In ethylene in the vapour phase the $\pi - \pi^*$ transition appears at 165 nm ($\epsilon_{\max} = 1000 \text{ m}^2 \text{ mol}^{-1}$). The transition is out of the normal range of most spectrometers.

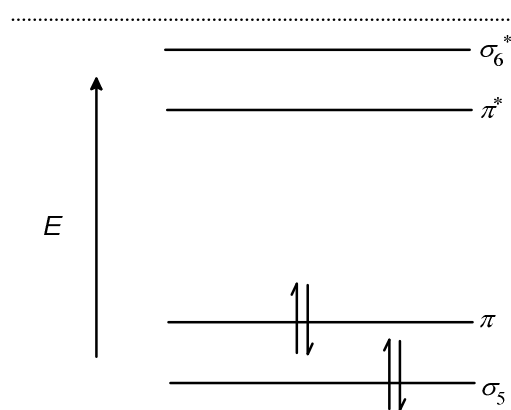


Fig. 12.1: Orbital energy diagram for ethylene.

Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift). The effect is progressive as the number of alkyl groups increases. Attachment of a heteroatom (bearing nonbonded electrons) to the ethylenic linkage also gives rise to a red or bathochromic

shift. Nitrogen and sulphur are the most effective heteroatoms shifting the absorption well into the near ultraviolet region. For example methyl vinyl sulphide ($\text{CH}_3\text{SCH}=\text{CH}_2$) absorbs at 228 nm. The absorptions of cyclic monoolefins resemble those of the open chain olefins and the absorption has no relationship to ring size. When there are two or more isolated ethylenic bonds in a molecule, it absorbs at the same position as the single ethylenic chromophore. The intensity of absorption, however, is proportional to the number of isolated chromophoric groups in the molecule.

As the absorption due to isolated ethylenic chromophore takes place in far ultraviolet region, electronic spectroscopy has thus little use in detecting isolated double bond. Conjugation markedly affects the position of absorption due to the >C=C< chromophore giving rise to a bathochromic shift. Thus, the λ_{max} value for $\pi - \pi^*$ transition for the 1,3-butadiene is 217 nm as compared to 185 nm for the 1,5-hexadiene.

$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$
1,3-butadiene	1,5-hexadiene
λ_{max} 217 nm	λ_{max} 185 nm
ϵ_{max} 2100 $\text{m}^2 \text{mol}^{-1}$	ϵ_{max} 2000 $\text{m}^2 \text{mol}^{-1}$

This relatively large increase in the wavelength of absorption due to conjugation can be explained as follows. In ethylene, the two $2p$ atomic orbitals combine to form a set of π and π^* molecular orbitals. In conjugated dienes such as 1,3-butadiene, when π and π^* molecular orbitals of two ethylenic linkages are close enough, overlap can occur. As a result, a combination of two π molecular orbitals gives two delocalized orbitals of lower and higher energy (π_1 and π_2). Similarly the two π^* orbitals give rise to two delocalized π^* orbitals of different energies (π_3^* and π_4^*) (Fig.12.2). Thus, the lowest energy $\pi_2 - \pi_3^*$ transition in 1,3-butadiene occurs at a longer wavelength (217nm) as compared to the lowest energy $\pi - \pi^*$ transition of 1,5-hexadiene (185 nm).

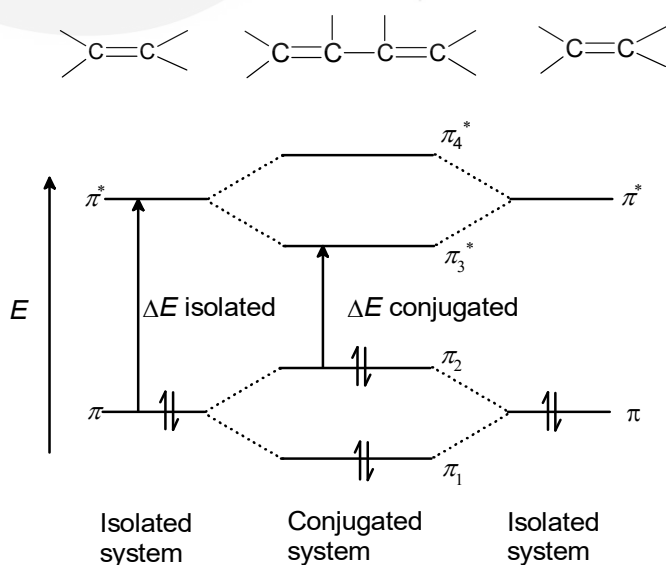


Fig. 12.2: Molecular orbital energy relationship between π -orbitals of isolated and conjugated dienes.

As the extent of conjugation increases, it lowers still further the energy of transition from the highest occupied π orbital to the lowest unoccupied π^* orbital, thereby the λ_{\max} value increases.

Table 12.1 gives the wavelengths of some conjugated polyenes that demonstrate this effect.

Table 12.1: Absorption bands of conjugated polyenes $\text{H}(\text{CH}=\text{CH})_n\text{H}$

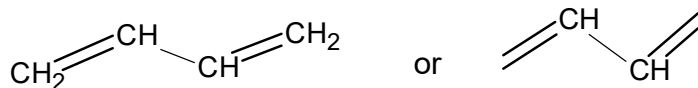
n	λ_{\max}/nm
2	217
3	268
4	304
5	334
6	364
11	390
8	410

The effects of substituents and geometry on the absorption bands of conjugated dienes are fairly consistent. A set of empirical rules has been formulated by Woodward to predict the absorption of open chain (acyclic) and six-membered ring dienes. These rules have been modified by Feiser and Scott. The rules are summarised in Table 12.2.

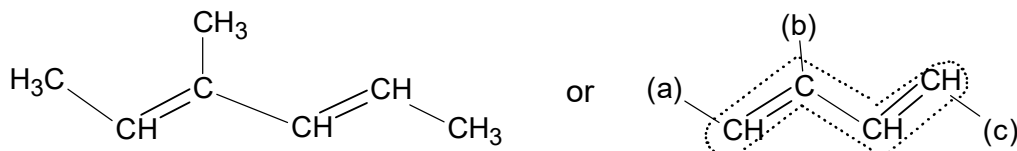
Table 12.2: Woodward Rules for predicting $\pi - \pi^*$ Absorption in Dienes

Value assigned to parent open chain diene		217 nm	
Value assigned to parent heteroannular diene		214 nm	
Value assigned to parent homoannular diene		253 nm	
Increments for			
a)	each alkyl substituent or ring residue	5 nm	
b)	each exocyclic double bond	5 nm	
c)	Each double bond extending conjugation	30 nm	
d)	auxochrome	- O(acyl)	0 nm
		-O(alkyl)	6 nm
		-S(alkyl)	30 nm
		-Cl, -Br	5 nm
		-N(alkyl) ₂	60 nm
		Calculated $\lambda_{\max} =$	Total

In order to be able to apply these rules you must be able to identify the type of structures referred to in Table 12.2. The basic chromophore unit is a 1,3-butadiene which is considered the parent acyclic (or non-cyclic) diene:



If saturated alkyl groups are attached to the diene, then an additional contribution for each group is added, e.g., $\pi-\pi^*$ absorption in 1,2,4-trimethylbutadiene(I) is analysed in terms of the rules as follows:



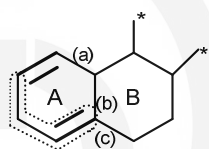
Base value for acyclic diene (I) = 217 nm

For three methyl groups, add $3 \times 5 = +15$ nm

Predicted λ_{max} for $\pi-\pi^*$ transition = 232 nm

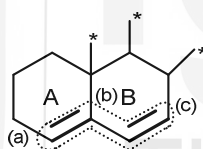
Observed λ_{max} for $\pi-\pi^*$ transition = 231 nm

If the diene system is contained in a single ring, it is termed homoannular, e.g., compound (II). On the other hand if it is spread over two rings, it is said to be heteroannular, e.g., compound (III).



(II)

Homoannular diene



(III)

Heteroannular diene

For compound (II) we have a base value of = 253 nm

For three ring residues (a), (b) and (c): add 3×5 nm = +15 nm

The lower double bond in A is attached to but is outside ring B, i.e., it is exocyclic to ring B: add 5 nm = +5

Predicted λ_{max} value = 273 nm

Observed λ_{max} value = 275 nm

Note that the groups marked with a * do not contribute as they are not directly attached to the diene system.

For compound (III) we have a base value of = 214 nm

For three ring residues (a), (b) and (c): add 3×5 nm = +15 nm

The double bond in ring A is in exocyclic position to ring B: add 5 nm = +5

Predicted λ_{max} value = 234 nm

Observed λ_{max} value = 235 nm

Thus in all the three cases, the predicted λ_{\max} values are in very good agreement with the observed values.

SAQ 1

Why the λ_{\max} value for $\pi - \pi^*$ transition for the 1, 3-butadiene is 217 nm as compared to 185 nm for the 1,5-hexadiene?

12.2.2 Acetylenic and Benzenoid Chromophore

The electronic spectra of the acetylenic and benzenoid chromophores are more complex than those of the ethylenic chromophore. These cannot be explained by following the model presented for the ethylenic chromophore. They exhibit three absorption bands each as shown below.

Acetylene: 152 nm (strong), 182 nm (moderate), 220 nm(weak)

Benzene: 184 nm (strong), 204 nm (strong), 254 nm (weak).

In each case, you can see, the lowest energy absorption band is weak, which is characteristic of a forbidden transition, e.g., $n - \pi^*$. But there are no non-bonding electrons in these molecules. Thus all the three transitions arise from $\pi - \pi^*$ transitions. Acetylene and benzene are highly symmetrical molecules having degenerate molecular orbitals. Transitions between degenerate orbitals in these cases give rise to the complexity in their electronic spectra.

12.2.3 Carbonyl Chromophore

You know that the carbonyl group contains, in addition to a pair of σ electrons, a pair of π electrons and two pairs of nonbonding electrons. Saturated aldehydes and ketones exhibit three absorption bands due to $\pi - \pi^*$, $n - \sigma^*$ and $n - \pi^*$ transitions (Fig. 12.3)

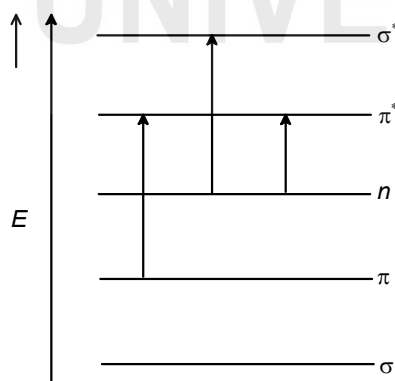


Fig. 12.3: Electronic transitions of a carbonyl group in aldehyde and ketones.

Two bands appear in the far ultraviolet region near 150 nm and 190 nm region and are due to the $\pi - \pi^*$ and $n - \sigma^*$ transitions, respectively. The third band is due to the forbidden $n - \pi^*$ transition which appears as a weak band ($\epsilon_{\max} < 3.0 \text{ m}^2 \text{ mol}^{-1}$) in the near ultraviolet region in the 270-300 nm region. In formaldehyde the $n - \pi^*$ absorption band is found at 310 nm. In contrast to the situation in alkenes, alkyl substitution moves this absorption to higher energy. Thus in acetaldehyde and acetone this band appears at 290 nm and 279 nm,

respectively. Auxochromes such as Cl, OH and NH_2 cause a larger shift in the carbonyl $n - \pi^*$ absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect (π -electron release) of the lone pair of the substituent raises the energy of the π^* orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (Fig. 12.4 (a)). The negative inductive effect (σ -electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (Fig. 12.4 (b)). The overall shift arises from the sum of these two effects.

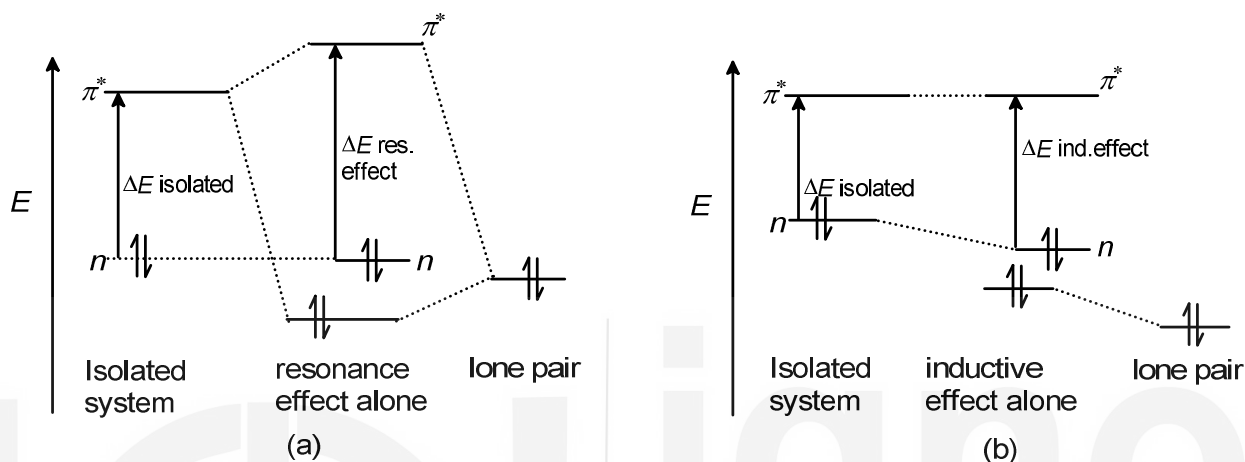


Fig. 12.4: Schematic diagram of a) the resonance effect alone and b) the inductive effect alone of a substituent on the $n - \pi^*$ transition of a carbonyl group.

When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond ($\text{C}=\text{C}$), the compound is known as an enone or α, β -unsaturated ketone, e.g., methyl vinyl ketone ($\text{CH}_3\text{COCH}=\text{CH}_2$). Conjugation has an effect on the energy of $\pi - \pi^*$ transition similar to that in alkenes. As the energy of the π^* orbital is lowered by conjugation (Fig. 12.5), the $\pi - \pi^*$ and $n - \pi^*$ absorptions move to longer wavelengths. Thus for propenal ($\text{CH}_2=\text{CH}-\text{CHO}$), the $\pi - \pi^*$ and $n - \pi^*$ absorptions occur at 202 nm and 336 nm, respectively.

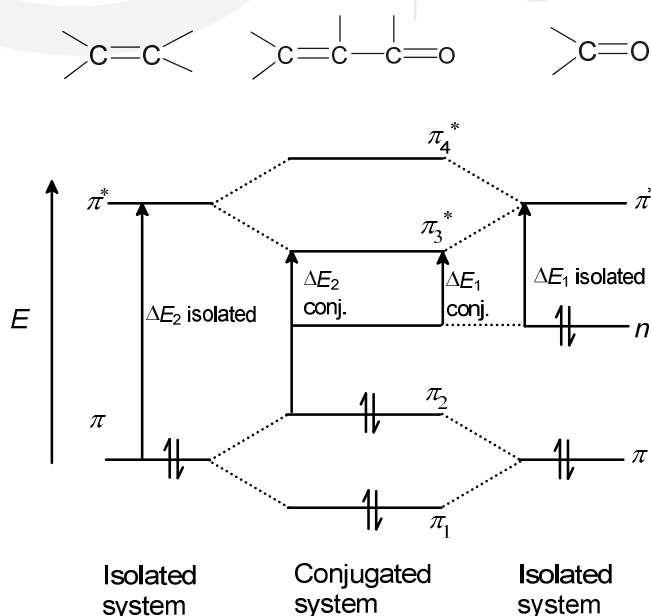
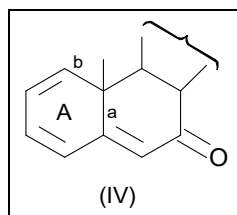


Fig. 12.5: Orbital energy relationships between isolated and conjugated $\text{C}=\text{C}$ and $\text{C}=\text{O}$ groups.

As with the conjugated dienes, there are empirical rules to predict the position of the $\pi - \pi^*$ band in enones. These rules were put forth by Woodward and modified by Feiser and Scott. These rules are summarised in Table 12.3.

We will now apply the rules for α, β -unsaturated ketones to predict the absorption maximum in compound IV.



Value for α, β -unsaturated ketones	= 215 nm
for β -substituent (marked a); add 12 nm	= + 12 nm
for α -substituent (marked b); add 18 nm	= + 18 nm
for two double bonds extending conjugation; add 2×30 nm	= + 60 nm
for homoannular diene component; add 39 nm	= + 39 nm
For exocyclic double bond; add 5 nm	= + 5 nm
calculated λ_{\max} value	= 349 nm

Three λ_{\max} values have been observed for this compound and these are 230 nm, 278 nm and 348 nm. The longest wavelength peak is in excellent agreement with the calculated value.

Table 12.3: Feiser and Scott rules for predicting $\pi - \pi^*$ absorption in α, β -unsaturated ketones (enones) and aldehydes

Value for parent acyclic ketone		215 nm	
Value for parent six-membered ring ketone		215 nm	
Value for parent five-membered ring ketone		202 nm	
Value for parent unsaturated aldehyde		207 nm	
Increments for			
a)	each of double bond extending the conjugation	30 nm	
b)	each alkyl group or ring residue	α 10 nm	
		β 12 nm	
		γ and higher 18 nm	
c)	auxochromes	(i) -OH	α 35 nm
			β 30 nm
			δ 50 nm
		(ii) -OAc	α, β, δ 6 nm
			(iii) -OMe
		β 30 nm	
		γ 17 nm	
		δ 31 nm	
		(iv) -Salk	85 nm
		(v) -Cl	α 15 nm
			β 12 nm
		(vi) -Br	α 25 nm
			β 30 nm
		(vii) NR ₂	β 95 nm

d)	exocyclic double bond	5 nm
e)	homodiene component	39 nm
	Calculated λ_{\max} value	= Total

The next section describes the effect of solvent on electronic spectra.

SAQ 2

Explain with the help of a diagram the orbital energy relationships between isolated and conjugated C=C and C=O groups.

12.3 SOLVENT EFFECTS ON ELECTRONIC SPECTRA

As with vibrational spectra, the phase of the sample or the solvent used while measuring the spectrum can make a marked difference to the electronic spectra. Broadly, there are two extremes; the vapour phase and non-polar solvents on the one hand, and polar and hydroxylic solvents on the other. Let us consider the effect of solvents on $\pi - \pi^*$ and $n - \pi^*$ transitions one by one.

$\pi - \pi^*$ transitions

When a polar solvent is used, the dipole-dipole interaction with the solvent molecules lowers the energy of the excited state more than that of the ground state (Fig. 12.6). This is due to the fact that excited states are more polar than ground states. The energy difference between the excited and ground states is reduced. This leads to a small red shift of the absorption maximum in polar solvents. Thus the $\pi - \pi^*$ transition shows a red shift of the order of 10-20 nm when the solvent is changed from hexane to ethanol.

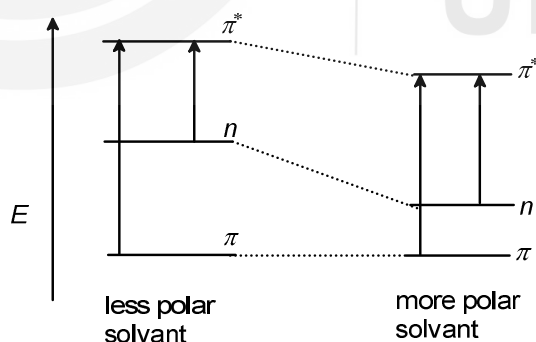


Fig. 12.6: Solvent effects on $n - \pi^*$ and $\pi - \pi^*$ transition.

$n - \pi^*$ transitions

Solvent effect for $n - \pi^*$ transitions is opposite to that found for $\pi - \pi^*$ transitions. Polar solvents cause a shift to lower wavelengths (blue shift) relative to non-polar solvents or the vapour phase. The effect is particularly pronounced in hydroxylic solvents. The lone-pair electrons in the non-bonding orbital hydrogen bond or otherwise interact strongly with the polar solvent, leading to a lowering in energy of the non-bonding orbital whereas π^* orbital is

affected much less (Fig.12.6). The result is an increase in the transition energy on going from a less polar to a more polar solvent. For example, in hexane solution, acetone shows absorption maximum at 279 nm whereas in aqueous solution, the absorption maximum is at 264.5 nm.

SAQ 3

Fill in the blanks in the following statements using the words given below:

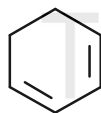
Polar, red, increased, decreased

- The $\pi - \pi^*$ transition shows a _____ shift in more polar solvents.
- The $\pi - \pi^*$ transition shows a blue shift in more _____ solvents.
- Hyperchromic effect means that the intensity of an absorption is _____
- Hypochromic effect means that the intensity of an absorption is _____

12.4 REPRESENTATIVE PROBLEMS

In this section there are some representative problems based on UV-visible spectroscopy. Try to solve them on your own and then verify the solution.

Example 12.1: Which molecule absorbs at the longer wavelength, 1,3-hexadiene or 1,4-hexadiene?



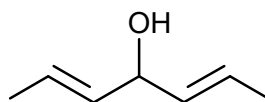
1,3-hexadiene



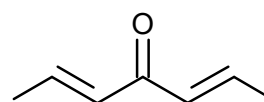
1,4-hexadiene

Solution: 1,3 hexadiene is conjugated and so absorbs at longest wavelength.

Example 12.2: Which of the following two molecules absorbs at the longer wavelength?



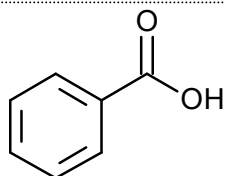
A



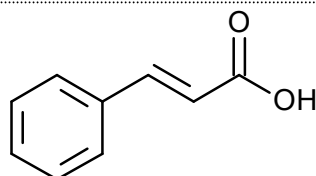
B

Solution: Generally, the more the conjugation length, the higher the λ_{\max} . B (the ketone participates in conjugation, while the carbon with the alcohol (A) does not), so B will absorb at longer wavelength.

Example 12.3: Benzoic acid has an absorption maximum at 230 nm. Where do you expect to see the absorption maximum in cinnamic acid?



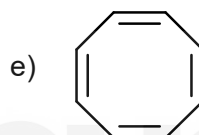
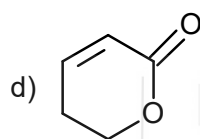
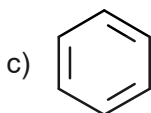
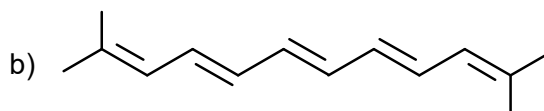
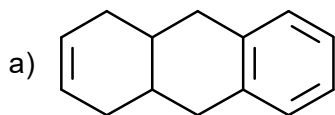
benzoic acid



cinnamic acid

Solution: Add another 30 or 40 nm due to conjugation and you get 260 or 270 nm.

Example 12.4: Which of the following compounds is most likely to absorb the visible region of the electromagnetic spectrum?

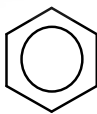
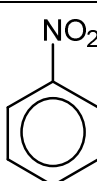


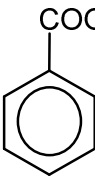
Solution: B as the length of its conjugation is quite large.

Example 12.5: Which of the following compounds absorbs UV radiation?

Heptane, benzene, butadiene, water, 1-heptene, nitrobenzene, benzoic acid.

Solution:

S. No.	Name	Structure	Type of Transmission
1.	Heptane	$\text{CH}_3-(\text{CH}_2)_3-\text{CH}_3$	$\sigma \rightarrow \sigma^*$ transition (No absorption, need very high energy)
2.	Benzene		$\pi \rightarrow \pi^*$ transition
3.	Butadiene	$\text{CH}_2=\text{CH}-\text{XH}=\text{CH}_2$	$\pi \rightarrow \pi^*$ transition
4.	Water	H_2O	$\sigma \rightarrow \sigma^*$ transition
5.	1-heptene	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}_2$	$\pi \rightarrow \pi^*$ transition
6.	Nitrobenzene		$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition

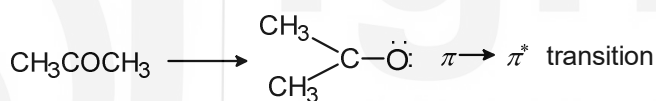
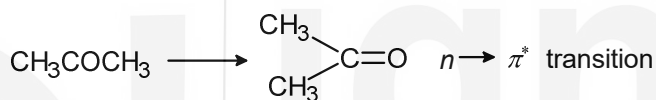
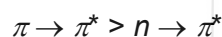
7.	Benzoic acid		$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition
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Example 12.6: UV spectrum of acetone (CH_3COCH_3) shows two peaks at $\lambda_{\text{max}} = 189 \text{ nm}$ and $\lambda_{\text{max}} = 273 \text{ nm}$. Identify the electronic transitions for each peak.

Solution:

- Higher wavelength, have less energy, show $n \rightarrow \pi$ transition ($\lambda_{\text{max}} = 273 \text{ nm}$).
- Lower wavelength, have high energy, show $\pi \rightarrow \pi^*$ transition ($\lambda_{\text{max}} = 189 \text{ nm}$).

We know that

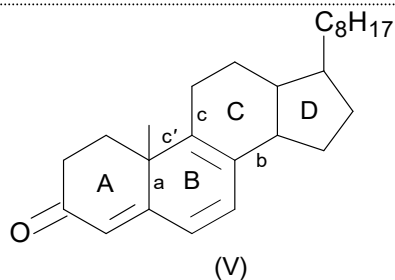


12.5 SUMMARY

In this unit, you have learnt how to identify small organic compounds, specially those with conjugated dienes, with the help of UV-visible spectroscopy. Discussions on the Woodward rules to predict absorption maxima in conjugated dienes, trienes and α , β -unsaturated aldehydes and ketones have been included. Lastly the effect of solvent on $n - \pi^*$ and $\pi - \pi^*$ transitions in carbonyl and unsaturated compounds and problems based on these have also been discussed.

12.6 TERMINAL QUESTION

- Most spectrometers cannot detect the wavelength of ethylene but can do so when there is an alkyl substitution of the ethylenic compound, why?
- Explain with the help of a diagram the resonance and the inductive effect of a substituent on the $n - \pi^*$ transition of a carbonyl group.
- Will nitrobenzene absorb UV radiations? Justify.
- Calculate the λ_{max} for the unsaturated ketone (V).



12.7 ANSWERS

Self-Assessment Questions

- This relatively large increase in the wavelength of absorption is due to conjugation and can be explained as follows. In ethylene, the two $2p$ atomic orbitals combine to form a set of π and π^* molecular orbitals. In conjugated dienes such as 1,3-butadiene, when π and π^* molecular orbitals of two ethylenic linkages are close enough, overlap can occur. LCAO of two π molecular orbitals gives two delocalized orbitals of lower and higher energy (π_1 and π_2). Similarly the two π^* orbitals give rise to two delocalized π^* orbitals of different energies (π_3^* and π_4^*) (Fig.12.2). Thus, the lowest energy $\pi_2 - \pi_3^*$ transition in 1,3-butadiene occurs at a longer wavelength (217nm) as compared to the lowest energy $\pi - \pi^*$ transition of 1,5-hexadiene (185 nm).
- When a carbonyl group of a ketone is conjugated with a carbon-carbon double bond (>C=C<), the compound is known as an enone or α , β -unsaturated ketone, e.g., methyl vinyl ketone ($\text{CH}_3\text{COCH}=\text{CH}_2$). Conjugation has an effect on the energy of $\pi - \pi^*$ transition similar to that in alkenes. As the energy of the π^* orbital is lowered by conjugation (Give Fig.12.5), the $\pi - \pi^*$ and $n - \pi^*$ absorptions move to longer wavelengths. Thus for propenal ($\text{CH}_2=\text{CH}-\text{CHO}$), the $\pi - \pi^*$ and $n - \pi^*$ absorptions occur at 202 nm and 336 nm, respectively.
- a) red b) polar c) increased d) decreased

Terminal Questions

- Alkyl substitution of the ethylenic compound moves the absorption to longer wavelengths (bathochromic shift) which is detectable by most spectrophotometers.
- Auxochromes such as Cl, OH and NH_2 cause a larger shift in the carbonyl $n - \pi^*$ absorption to shorter wavelengths. The shift in absorption results from a combination of resonance and inductive effects. The resonance effect (π -electron release) of the lone pair of the substituent raises the energy of the π^* orbital, but leaves the nonbonding electrons of the carbonyl group unchanged in energy (give Fig. 12.4 (a)). The negative inductive effect (σ -electron withdrawal) lowers the energy of the nonbonding orbital by making the carbon atom of the group more positive (give Fig. 12.4 (b)). The overall shift arises from the sum of these two effects.

3. Yes. Nitrobenzene will absorb UV radiations as it shows $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.
4. Base value for α, β -unsaturated ketone = 215 nm
- for two double bonds extending conjugation, add (2×30) = + 60 nm
- for ring residue β (marked a), add 1 × 12 nm = + 12 nm
- for ring residue (marked b), add 1 × 18 nm = + 18 nm
- for ring residue (marked c and c'), add 2 × 18 nm = + 36 nm
- for one exocyclic double bond in ring marked A, add 1×5 nm = + 5 nm
- for homodiene component, add 1 × 39 nm = + 39 nm
-
- Calculated λ_{\max} = 385 nm



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