Solvent Effects:-

Since the polarity of a molecule usually changes with electronic transitions, the position and the intensity of absorption maxima may be shifted by changing solvent polarity

(i) $\pi \rightarrow \pi^*$ Transitions.

Owing to non-polar nature of hydrocarbon double bonds the $\pi \rightarrow \pi^*$ transitions of alkene, dienes & polyenes are not appreciably affected by changing solvent polarity.

π-π^* transition of polar Compounds are shifted to longer wavelength and genrally towards higher intensity with increasing solvent polarity the excited state in this transition is more polar than the ground state, thus, dipole-dipole interaction with a polar solvent lowers the energy of the excited

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state more than that of ground state. Thus there is a bathochromic shift of 10-20nm in going from hexane as a solvent to ethanol i.e., on increasing solvent polarity.

In case of heteroaromatic Compounds which shows a marked hyperchromic shift on increasing solvent polarity.

(ii) $n \rightarrow \pi^*$ transition:-

On increase in solvent polarity usually shifts $n \rightarrow \pi^*$ transitions to shorter wavelength (high energy) Acetone shows λ_{max} 279nm in hexane, in water it shows λ_{max} 264.5nm

This can be explained on the basis that Carbonyl group is more polar in the ground state ($>C^{\delta+}-O^{\delta-}$) than in excited state ($>C^{\delta-}-O^{\delta+}$). Thus dipole-dipole interaction or hydrogen bonding with a polar solvent lowers the energy of the ground state more than the excited state resulting in hypsochromic shift in case of unconjugated as well as conjugated Carbonyl Compounds with increasing solvent polarity.

(iii) $n \rightarrow \sigma^*$ transitions:-

These transitions are affected by solvent polarity, specially by solvents capable of forming hydrogen bonds with protic solvents. Such associations involve non-bonding electrons of the heteroatom. The involvement of non-bonding electrons in hydrogen bonding lowers the energy of n-orbital and thus excitation of these electrons requires greater energy resulting in the hypsochromic shift with increasing polarity.

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* Polar Solvents stabilize polar groups through dipole-dipole interaction or hydrogen bonding
* If a chromophore is more polar in the ground state than in the excited state, then polar solvents stabilize the ground state to the greater extent than the excited state. Thus there is a hypsochromic shift with increasing solvent polarity.
* If a chromophore is more polar in the excited state than in the ground state, then the former is stabilized to a greater extent by polar solvents than the latter. Thus, there is a bathochromic shifts with increasing solvent polarity.

* It has been found that an increase in solvent polarity usually shifts $n \rightarrow \pi^*$ & $n \rightarrow \sigma^*$ bands to shorter wavelength & $\pi - \pi^*$ bands of polar compounds to longer wavelength.

Applications of Ultraviolet & Visible Spectroscopy

(1) Detection of a functional group:-
The presence or absence of a particular chromophore may be indicated by the presence or absence of an absorption band in the expected region.
For example, the presence of a low intensity band in the region 270-300nm indicates the presence of an aldehyde or ketonic carbonyl group. If the spectrum is transparent above 200nm, it shows the absence of
(1) an aldehydic or ketonic carbonyl group
(2) A conjugated system
(3) an aromatic ring

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① A bromine or iodine atom in the molecule.

② Detection of Conjugation and Elucidation of its Nature:-
Compounds containing a Conjugated System including aromatics are Characterised by their absorptions above 200nm. The longer the Conjugated System, the longer is the wavelength of absorption, usually accompanied by increased intensity. Also Substitution on a Conjugated System generally cause bathochromic and hyperchromic effects. Thus we can elucidate the nature of Conjugation by comparing values of λmax & εmax for the Compound under study with that of a probable analogous Compound.

③ Study of Extent of Conjugation

The value of λmax and εmax increases as the number of Conjugated multiple bonds increases, thus extent of Conjugation can be estimated. It has been found that the absorption occurs in the visible region if a polyene has eight or more Conjugated double bonds. A polyene with sufficient Conjugation becomes Coloured,
Ex: β-Carotene (orange) and lycopene (red) having eleven Conjugated double bonds are Coloured and absorb in the visible region at 450nm εmax 14×10^4 & 474nm εmax 18.6×10^4 respectively.

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(4) Distinction Between Conjugated and Unconjugated Compounds:-

In general, electronic Spectroscopy can distinguish isomeric Conjugated and unconjugated Compounds.

Ex- Isomeric diene 2,4 hexadiene & 2,5-hexadiene can readily be differentiated because the former being Conjugated diene will absorb over 200nm (227nm) where as latter being an unconjugated diene will absorb below 200nm (<175nm)

Similarly, an α,β-unsaturated ketone can be readily distinguished from β,γ-isomer because the former having Conjugated System will show both the $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$ transition bands at longer wavelengths Compared to that of the latter which is unconjugated Compound.

(5) Study of strain:-

The degree of Conjugation may suffer in strain molecules i.e, loss of π-orbital overlap in 2-Substituted biphenyls (there is steric strain which forces the rings out of Co-planarity resulting in the loss of Conjugation.)

This Causes hypsochromic and hypochromic effects which are measures of steric strain in such molecules i.e the larger are these effects, the greater will be the steric strain.

(6) Determination of Configuration of Geometrical Isomers:-

The cis-isomers in which groups are Closer to each other to cause steric strain and force the groups out of Co-planarity. Thus cis-isomer absorb at shorter wavelength & have lower intensity than

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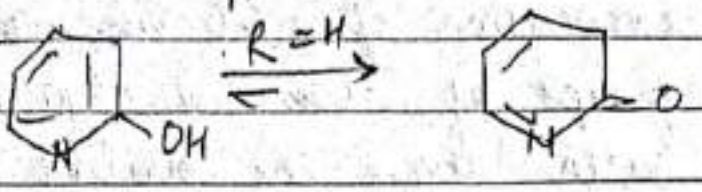
trans isomers

Ex cis Stilbene λ_{max} 283nm ϵ_{max} 12300

trans Stilbene λ_{max} 295nm ϵ_{max} 25000

⑦ Study of Tautomerism:-

UV Spectroscopy can be used to identify stable tautomeric species



2-Hydroxypyridine pyridin-2-one

Equilibrium has been shown to lie far to the right i.e the ultraviolet spectrum of the solution resembles that of a solution of N-methylpyrid-2-one (R=Me) and is different from that of 2-methoxypyridine (R=Me)

In this equilibrium α,β unsaturated ketone predominates.

⑧ Study of structural features in Different Solvents

In Certain Cases, the structure of a Compound changes with the change in the Solvent.

For example:- Chloral hydrate shows an absorption λ_{max} at 290nm (R band) but this band disappears when the spectrum is recorded in aq. solution. This shows that Compound has a Carbonyl group in hexane solution and its structure is $CCl_3CHO \cdot H_2O$ whereas in aq. medium it changes to $Cl_3CH(OH)_2$

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Identification of a Chromophore :-

Simple Conjugated Chromophore i.e., dienes and α,β unsaturated ketones have ε values of 10000-20000. The longer simple conjugated system have principle maxima with correspondingly higher ε values.

The presence of absorption band with ε value of 1000-10000 almost always indicate the pasence of an aromatic system.

Several unsubstituted aromatic systems display bands with these intensities, (bands) with a low transition probabilities low because of the symmetry of ground and excited state.

When the aromatic nucleus is substituted with groups which can extend the chromophore, strong bands appear with ε values above 10000, however bands with ε values below 10000 are generally present.

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