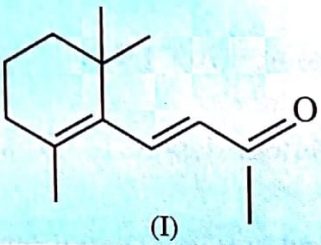
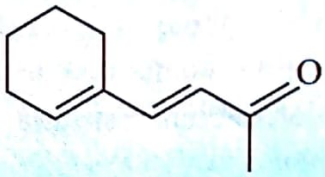


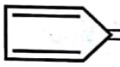
(I)



(II)

Ans. We see that the compound with λ_{max} 296 nm has half intensity as compared to the other compound. The decrease in intensity is due to steric hindrance by methyl group and its effect on the absorption of conjugated system. Thus, the compound I has decreased intensity.

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

Ans. The formula of fulvene is  $=CH_2$. It 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 is colourless.

26. o-Nitroacetanilide is deep yellow but para-nitro acetanilide is yellow. Why is the colour of 'o'-isomer deeper?

Ans. The ortho isomer exhibits intramolecular hydrogen bonding whereas the para Isomer shows intermolecular hydrogen bonding. Internal 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.

observed. The reason is that vibrational and rotational transitions.

2.33 Short Questions with Answers

1. Define the term 'spectroscopy'.

Ans. Spectroscopy involves the interaction between electromagnetic radiation and the substance under investigation.

2. Why is absorption and not emission spectroscopy used to study the spectra of organic compounds?

Ans. Emission spectroscopy cannot be used since the emission of radiation from an organic compound requires very high temperature. Organic compounds are low melting and thus generally decompose at high temperatures.

3. What is the effect of ultra-violet or visible light on the organic compound?

Ans. When the substance under investigation is subjected to the action of UV or visible radiation then it causes changes in the electronic energy levels within the molecule.

4. What do you mean by absorption of radiation in a spectrum or a record?

Ans. Absorption of radiation at a particular wavelength leads to decrease in the percent transmission to appear in the spectrum as a dip, called a peak or an absorption band.

5. What do you mean by a spectrum or record of the spectrum?

Ans. The spectrum of a compound represents a graph of either wavelength or frequency continuously changing over a small portion of the electromagnetic spectrum versus either percent transmission or absorbance.

6. Define Absorbance.

Ans. Absorbance is a measure of the absorption of radiation by a sample.

$$A = \log\left(\frac{\text{original intensity}}{\text{Intensity}}\right) = \log\frac{I_0}{I} = \in cl\,.$$

7. What is the effect of hydrogen bonding on ultra-violet absorption?

Ans. Hydrogen bonding shifts the ultra-violet absorptions to shorter wave lengths.

8. What do you mean by a good solvent in UV spectroscopy and what is its effect on absorption maximum?

Ans. A good solvent in ultra-violet or visible spectroscopy is one which is low priced and transparent down 210 nm. Polar bonds like carbonyl are affected by solvent polarity. With increase in solvent polarity, $n \rightarrow \pi^*$ transitions undergo blue shift (towards short wave length) while $\pi \rightarrow \pi^*$ transition undergo red shift.

9. Tell whether a molecule can undergo more than one electronic shift.

Ans. Depending upon the wavelength of light used, a molecule can undergo all the possible

electronic transitions. For example, acetaldehyde (CH_3CHO) can undergo $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ transitions.

10. What happens to the excited molecule when radiation is cut off?

Ans. In that case, the excited molecule gives off energy and returns to the ground state. The process is called deactivation. The excited molecule may undergo a chemical change depending upon the nature of the molecule. Cis-trans isomerisation is an example of the type.

11. For the detection of aldehydes and ketones, which transition is more authentic, $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$.

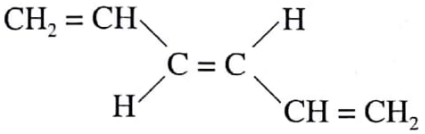
Ans. $n \rightarrow \pi^*$ with low value of extinction coefficient (ϵ_{max}).

12. Describe the shift in absorption ($n \rightarrow \pi^*$) when a more polar solvent is used.

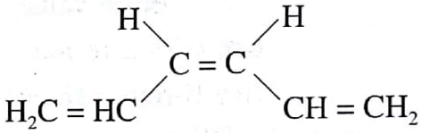
Ans. When a more polar solvent is used, the excitation of n electrons to π^* orbital requires more energy. Thus, the shift is towards shorter wavelength.

13. How will you distinguish between cis and trans-1, 3, 5-Hexatriene.

Ans. The structure of hexatrienes are:



(Trans)



(Cis)

cis-isomer absorbs at lower wavelength, because the bulky groups on the same side cause repulsive interactions resulting in the reduction in conjugation.

14. Which spin state is observed at the instant of excitation?

Ans. Excitation occurs very rapidly ($<10^{-13}s$) and thus, there is no time for the excited electron to change its spin (Franck Condon Principle). Clearly, singlet ground state (S_0), gives singlet excited state (S_1).

15. For which isomer, $\pi \rightarrow \pi^*$ transition occurs at high wavelength and higher extinction coefficient: cis-stilbene or trans-stilbene.

Ans. Trans-stilbene absorbs at higher wavelength. The reason is that coplanarity is needed for the most effective overlap of π-orbitals and thus, increased ease of $\pi \rightarrow \pi^*$ transition. It is possible in case of trans-isomer.

16. What structural features may produce bathochromic or hypsochromic effect in an organic compound?

Ans. A bathochromic or red shift is caused by the change of solvent or the presence of an auxochrome. A hypsochromic (or blue) shift is caused by the change of solvent or by the structural changes such as reduction in conjugation.

17. Aniline absorbs at 280 nm (ϵ_{max} 8600) but in acidic solution, the main absorption band is seen at 203 nm (ϵ_{max} 7500) which is comparable to benzene. Explain.

Ans. In the acidic medium, aniline is converted to anilinium ion. Thus, due to removal of conjugation of lone pair of electrons on nitrogen atom of aniline with π-bond system of benzene, the hypsochromic shift takes place.

18. Which out of benzene (colourless) or quinone (yellow) has more easily promoted electrons?

Ans. Quinone.

19. Why the λ_{max} for the diene (I) is observed at lower nm than II?