

Tutorial I

Spectroscopy (January 2023)

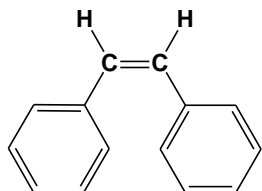
Answer Key

1. Explain why butadiene exhibits a higher value of λ_{\max} for π - π^* transition than that of ethylene.

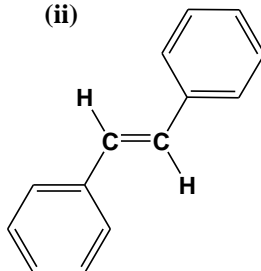
Energy gap between HOMO and LUMO is less in butadiene because of conjugation. Explain with the help of MO diagram.

2. How can you identify the cis-isomer from UV-Visible spectrum

(i)



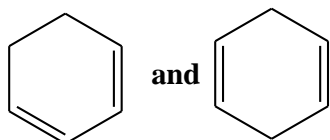
(ii)



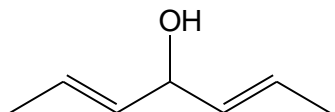
Steric hindrance is more in Cis isomer, conjugation will not be effective. In trans isomer, both the rings are in conjugation. λ_{\max} for π - π^* transition will be at a higher wavelength for trans isomer.

3. How can you distinguish between the following pairs of compounds using UV-Visible spectroscopy ?

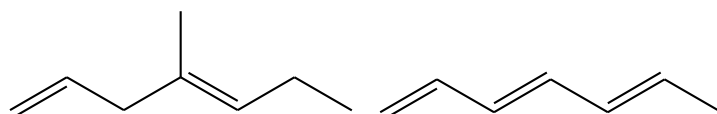
(i)



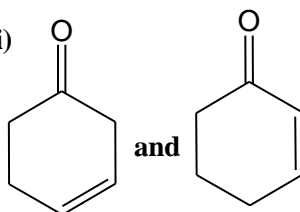
(iii)



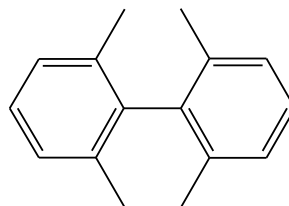
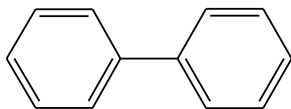
(iv)



(ii)



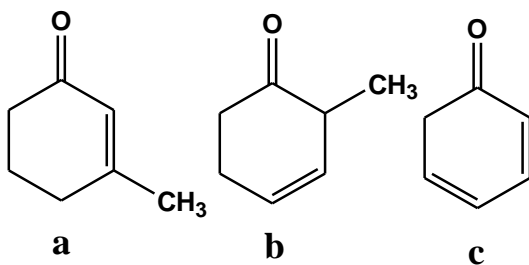
(v)



λ_{max} for π - π^* transition will be at a higher wavelength in (i) 1st (ii) 2nd (iii) 2nd (iv) 2nd (iv) 1st.

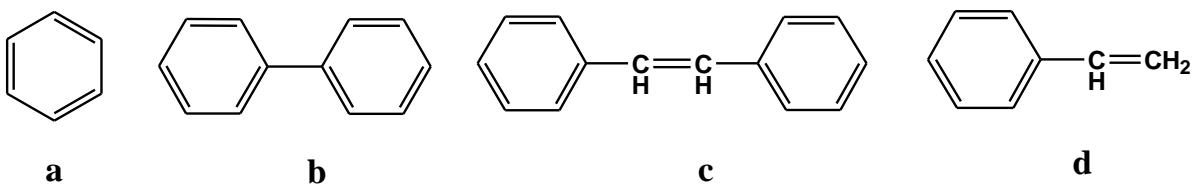
4. Rank the compounds in each group in the order of decreasing λ_{max} .

(i)



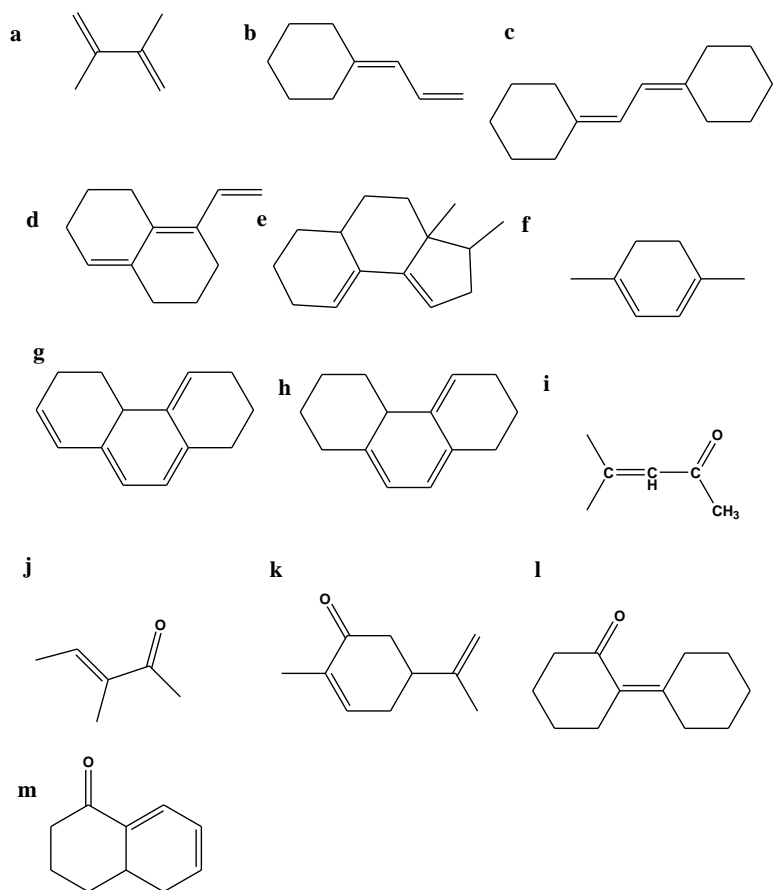
$c > a > b$

(ii)



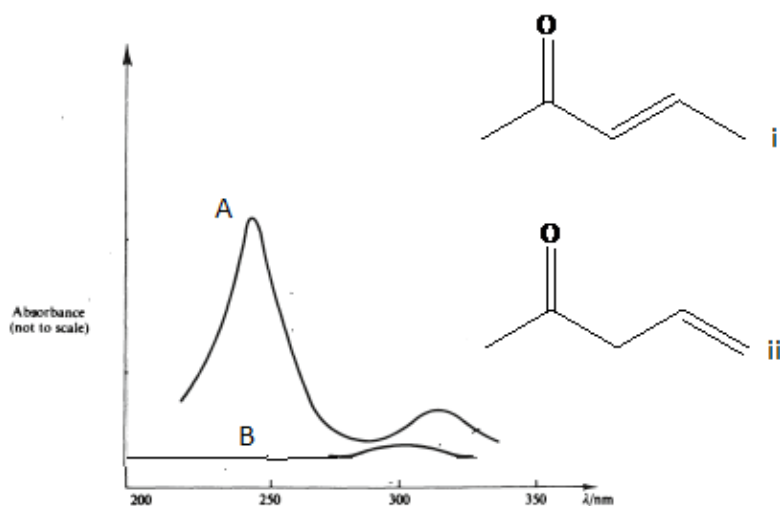
$c > b > d > a$

5. Calculate λ_{max} using Woodward-Fieser rules



a) 227 nm b) 222 nm c) 247 nm d) 277 nm e) 245 nm f) 273 nm g) 353 nm h) 323 nm i) 239 nm
 j) 237 nm k) 237 nm l) 259 nm m) 317 nm

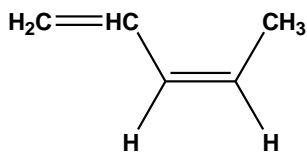
6. Assign the spectra to the following compounds



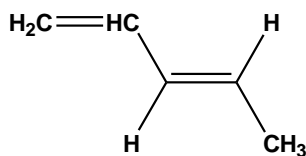
Spectrum A belongs to (i): The compound exhibits π - π^* transition and n - π^* transition. In compound (i) --C=O is in conjugation with the double bond. Hence both the transitions are visible in UV region (above 200 nm). The first peak which is of high intensity corresponds to π - π^* transition, the speak of very low intensity corresponds to n - π^* transition which is forbidden and happens at higher wavelength.

In compound (ii) --C=O is not in conjugation with the double bond, hence π - π^* transition will occur at a wavelength below 200 nm and is not visible in the UV-Visible spectrum. The peak of small intensity corresponds to the forbidden n - π^* transition which always happen above 200 nm.

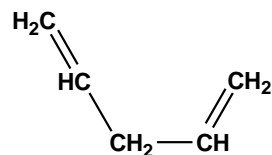
7. Assign with justification the λ_{max} values of 176, 211 and 215 nm to the dienes given below.



a



b



c

176 nm: C

211 nm : a

215 nm : b