Terms used in UV / Visible Spectroscopy

Chromophore

The part of a molecule responsible for imparting color, are called as chromospheres.

OR

The functional groups containing multiple bonds capable of absorbing radiations above 200 nm due to n → π* & π → π* transitions.

e.g. NO_2, N=O, C=O, C=N, C≡N, C=C, C=S, etc

Chromophore

To interpretate UV – visible spectrum following points should be noted:

1. Non-conjugated alkenes show an intense absorption below 200 nm & are therefore inaccessible to UV spectrophotometer.

2. Non-conjugated carbonyl group compound give a weak absorption band in the 200 - 300 nm region.

Chromophore

When double bonds are conjugated in a compound λ_{max} is shifted to longer wavelength.

e.g. 1,5 - hexadiene has λ_{max} = 178 nm

2,4 - hexadiene has λ_{max} = 227 nm

Auxochrome

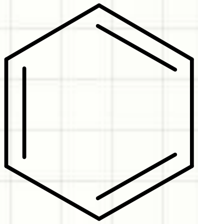
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

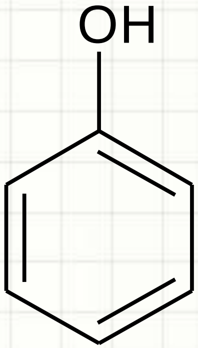
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

Auxochrome

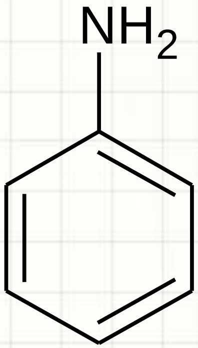
e.g. Benzene λ_{max} = 255 nm



Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



- Q: the anilinium ion shows λmax = 265nm. Explain.
- End absorption:
- Is an absorption that are increased in intensity towards shorter wave length due to n → δ* transition, occur near 200 nm with the molecule contain O, N, S or halogen atoms

1 • Bathochromic Shift (Red Shift)

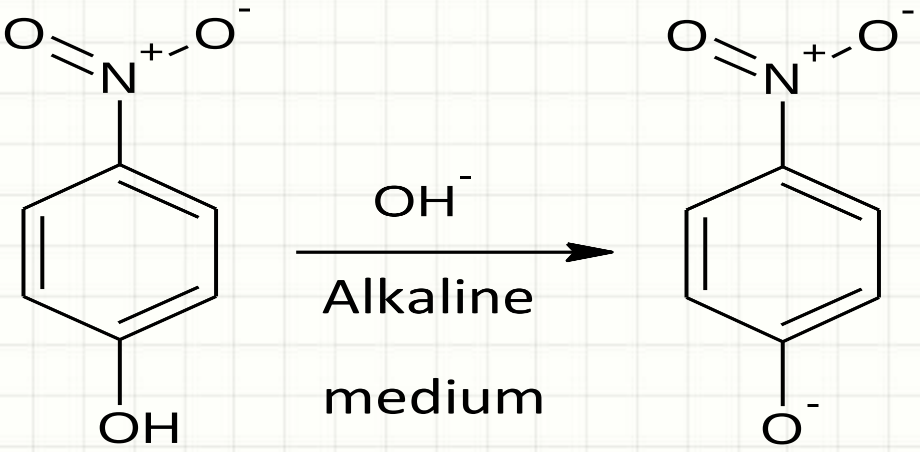
- When absorption maxima (λ_{max}) of a compound shifts to longer wavelength, it is known as bathochromic shift or red shift.

- The effect is due to presence of an auxochrome or by the change of solvent.

- e.g. An auxochrome group like –OH, -OCH_3 causes absorption of compound at longer wavelength.

1 • Bathochromic Shift (Red Shift)

- In alkaline medium, p-nitrophenol shows red shift. Because negatively charged oxygen delocalizes more effectively than the unshared pair of electron.



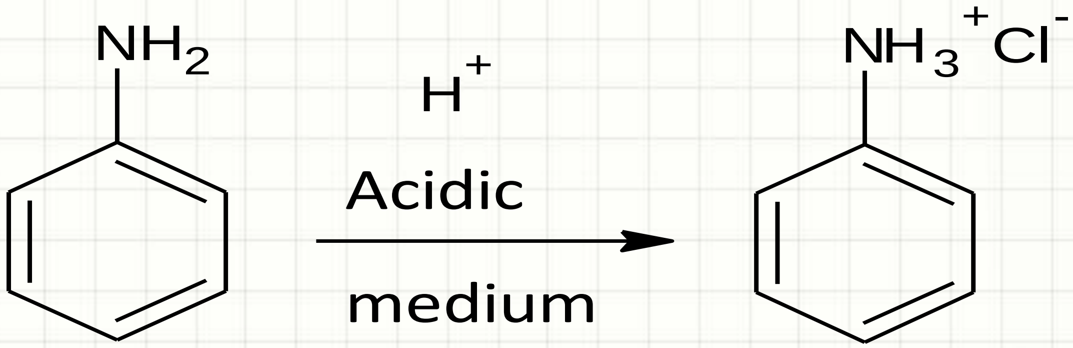
λ_{max} = less than λ_{max}

• Hypsochromic Shift (Blue Shift)

- When absorption maxima (λ_{max}) of a compound shifts to shorter wavelength, it is known as hypsochromic shift or blue shift.
- The effect is due to presence of an group causes removal of conjugation or by the change of solvent.

2 • Hypsochromic Shift (Blue Shift)

- Aniline shows blue shift in acidic medium, it loses conjugation.



Aniline

λ_{max} = 280 nm

λ_{max} = 265 nm

• Hyperchromic Effect

- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.

- If auxochrome introduces to the compound, the intensity of absorption increases.

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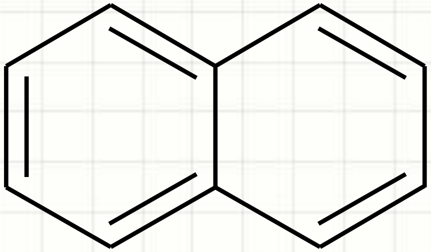
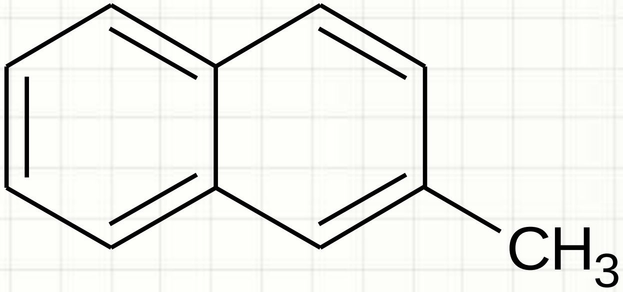
• Hypochromic Effect

- When absorption intensity (ε) of a compound is decreased, it is known as hypochromic shift.



Naphthalene

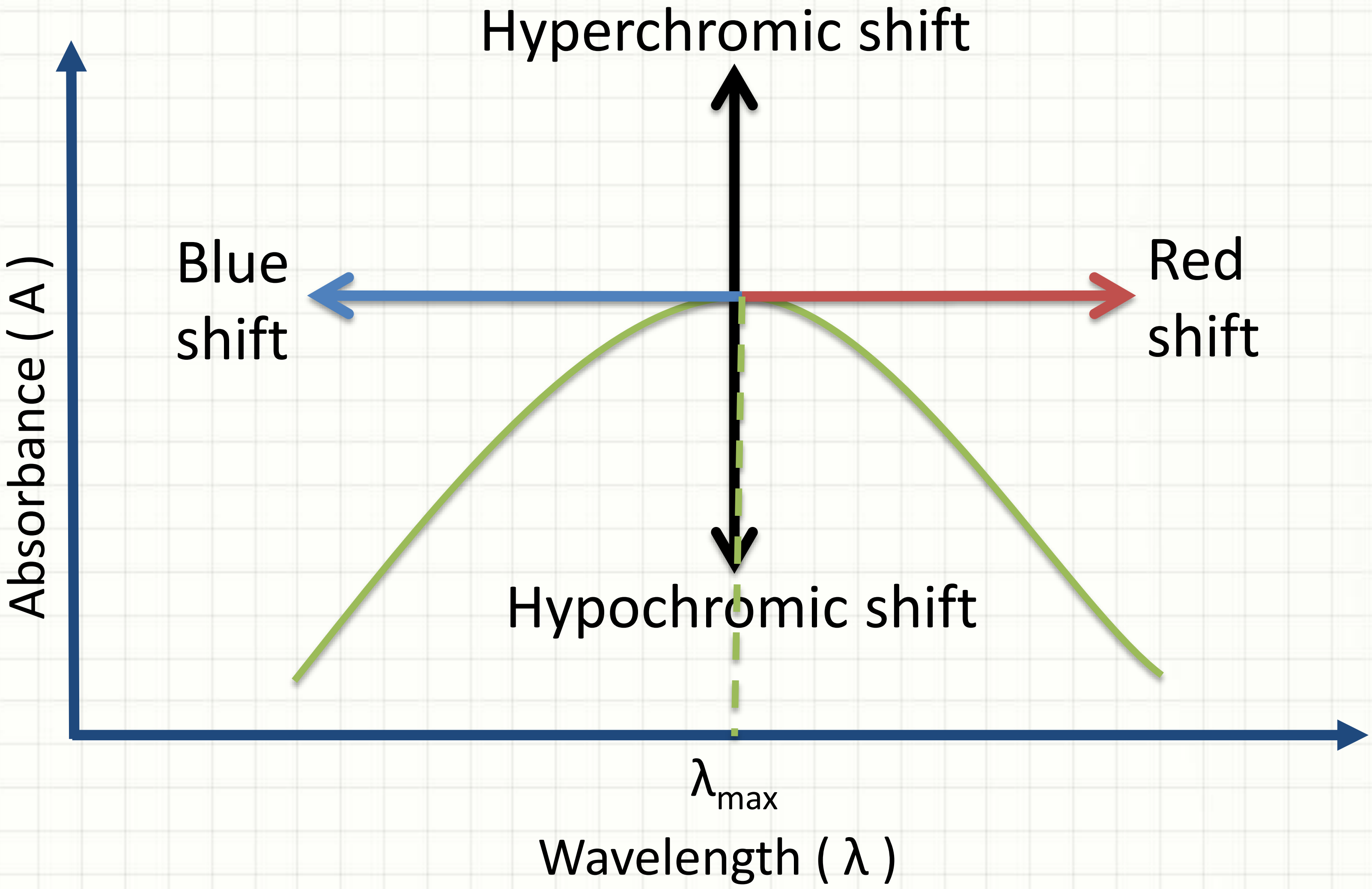
ε = 19000



2-methyl naphthalene

ε = 10250

Shifts and Effects



Phenyl compounds

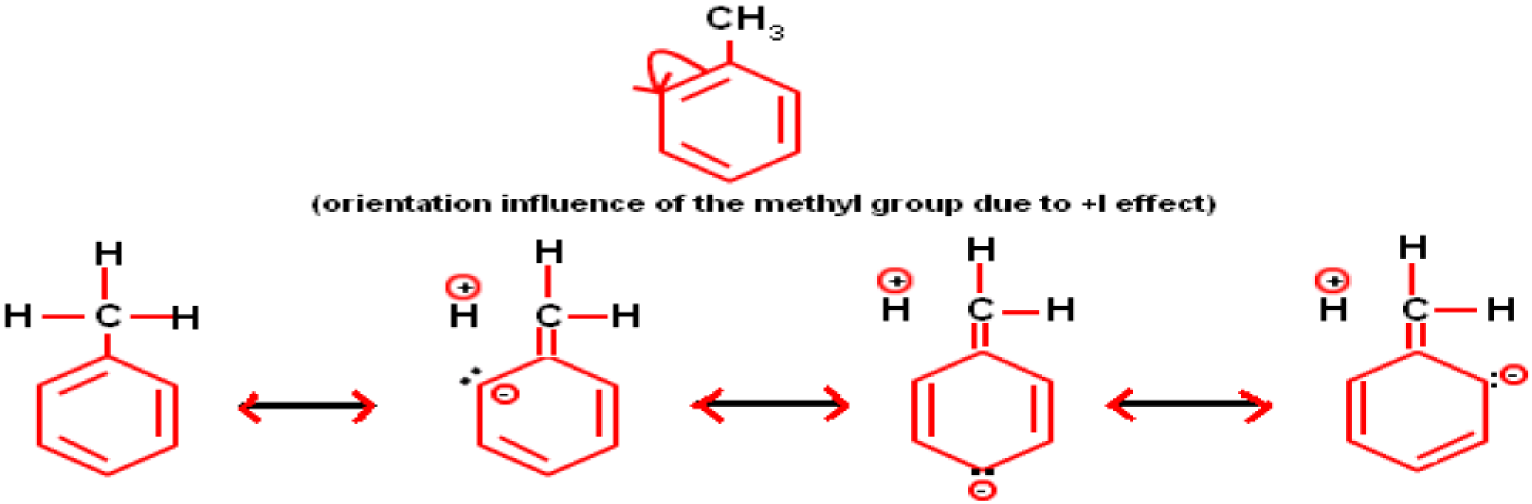
Benzene ring has 2 bands, primary band with high intensity λ max = 203.5 nm, secondary band with lower intensity λ max = 255 nm.
The secondary band and most aromatic hydrocarbon have the transition due to π to π* and sensitive to polarity of the solvent.

1. Monosubstituted benzene

benzene λ max value 255 nm, while λ max of Toluene is 261 nm due to resonance because of hyperconjugation between 6 bonds of alkyl and π bond of aromatic

1. Monosubstituted benzene

a. Alkyl substituted benzene e.g Toluene



(orientation influence of the methyl group due to +I effect)

(orientation influence of methyl group due to hyperconjugation)

λ max of Meta dimethyl substituted benzene is 262 nm.

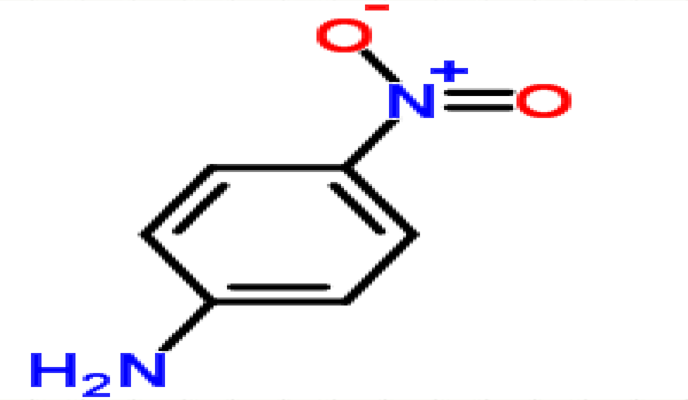
If ortho dimethyl substituted benzene, the λ max is 254 nm, this is because of steric hindrance that will lead to destruction of hyper conjugation

if di phenyl, the λ max become 252 nm this is because no co-planarity achieved (Not in the same plane).

b. Auxochromic substituted benzene contain NH_2, OH ….. Red shift occur due to n>>>δ* or n>>>π*.

2. Disubstituted Benzene

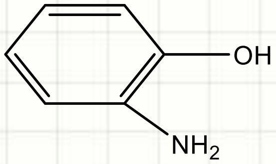
a) The disubstituted groups are electronically complementary (electron donating and electron with drawing group) and at para position



So, greater red shift in the mean absorption bonds compared to either one separately

λ max = 375 nm (note: λ max of amine is 280 nm) so, increase 95 nm due to greater extension of conjugation from the electron donating group to E.W.D group through benzene ring.

b) If disubstituted electronically not complementary and/or not on para position (Ortho, Meta) U.V will be close to that occur separately, not interacting chromophor. e.g. Ortho amino phenol λ max = 283 nm



Conjugated system:

Multiple bonds that are alternative with single bonds are said to be conjugated

Thus 1,3-butadiene ……… conjugated system.

1,4- pentadiene …… non conjugated system.

Characteristics of conjugated system:

More stable than non-conjugated one because during resonance there is transfer of electron and it will produce some partial double bond character between C2 and C3 thus strengthen C2-C3 bond and stabilizing the molecule.

$$C{=}C-C{=}C \leftrightarrow {}^{-}C-C{=}C-C^{+} \leftrightarrow {}^{+}C-C{=}C-C^{-} \rightarrow\rightarrow\rightarrow C \approx C \approx C \approx C$$

2- Many of the pigments responsible for the brilliant color of fruit and flowers are said to be conjugated polyene e.g: Lycopene.

Compound containing series of conjugated chromophore groups will appear colored to the eye So, absorbed at equal or more than 400 nm

If compounds appear colored contain not less than 4, usually 5 or more conjugated chromophoric and auxochromic groups except azo, diazocompounds .

3- conjugated system had to red shift (increase wave length) because the π electron spread over at least 4 atomic center

Generally conjugated system absorb 15 – 45 nm, longer wave length than non-conjugated system.

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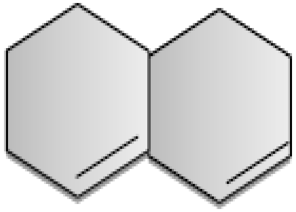
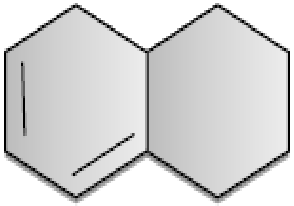
Diene which exist in 6 membered fused ring



Heteroamular

λ max =214 nm

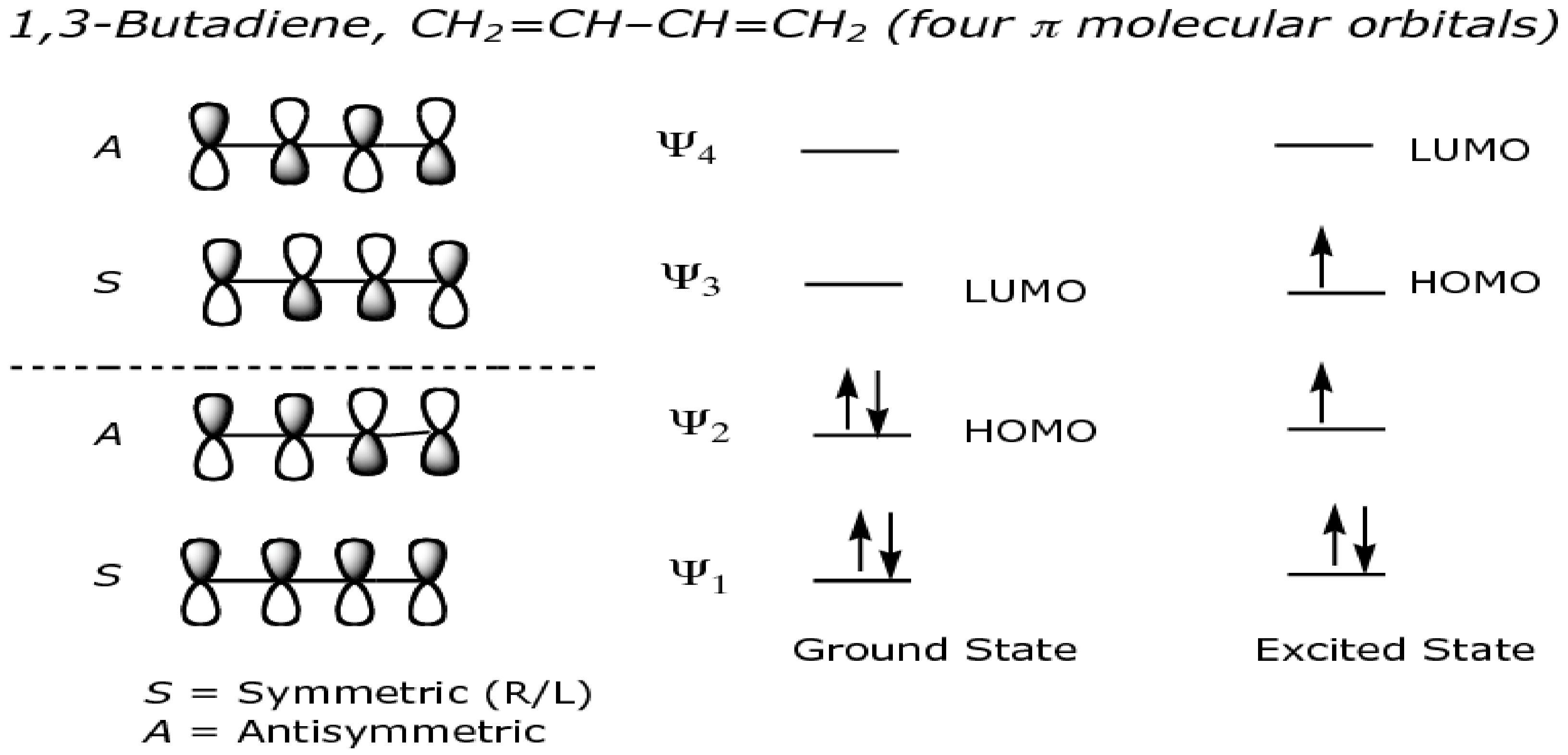


homoamular

λ max =253 nm

if two or more chromophoric group are present in a molecule and they are conjugated the effects are usually additives.

1,3-butadiene has 4 π molecular orbital two of them lower energy is required in ground state and two molecular orbital called Antibonding orbital



1,3-Butadiene, $CH_2{=}CH{-}CH{=}CH_2$ (four π molecular orbitals)

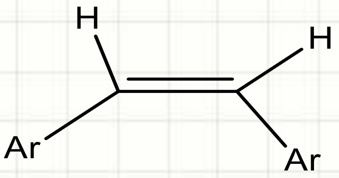
On irradiation with uv light, 1,3-butadiene absorbs energy and a π electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The exact wave length necessary to cause π to π* transition in a conjugated molecule depend on the gap between HOMO and LUMO which in turn depend on the nature of the conjugated system

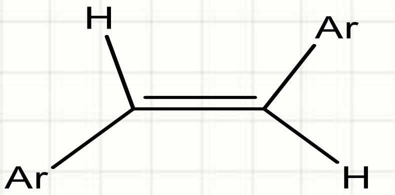
As a general rule the greater the extent of conjugation the less energy needed (longer wave length of radiation)

The wave length of 1,3-butadiene is 217 nm
The wave length of 1,3,5hexatriene is 253 nm.

Stereochemistry



cis isomer



transe isomer

Comparison between cis and trans:
1-Cis: Higher steric Hindrance, Less coplanarity, Blue shift, 283nm, more E.
2- Trans: Lower steric hindrance, More coplanarity, red shift, 295 nm, less E.

The absorption due to the π → π* transition of the transe isomer occur at longer wave length