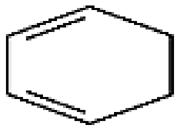
Spectroscopy (review)

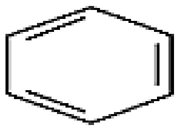
Partial structures :

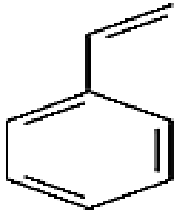
- ❖ Strong UV (ε > 1000):-

Conjugated π systems give ε > 1000.


ε = 20, 900


ε = 4,580


ε = 8,000

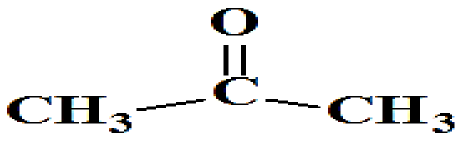

ε = 12,000

Q // If ε > 1000 , what kind of partial structure is indicated ?

- ✓ The compound MUST CONTAIN a conjugated π system.
- ✓ It might be aromatic (like benzene).
- ✓ It might be a conjugated polyene (like 1,3-butadiene).

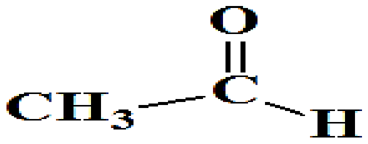
- ❖ Weak UV (ε < 100):

-Aldehydes or Ketones give e < 100



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

acetone ε = 19



$CH_3-\overset{\overset{O}{\|}}{C}-H$

acetaldehyde ε = 12

Q// If ε < 100 , what kind of partial structure is indicated ?

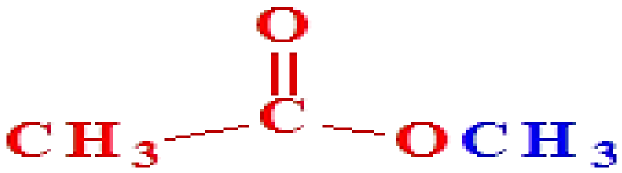
- ✓ The compound must have an aldehyde or ketone carbonyl.
- ✓ There is no heteroatom next to the carbonyl carbon (only C or H).

- ❖ UV End Absorption (No ε) **Esters give end absorption**

Q// If UV = end absorption, what partial structure is indicated?

- ✓ A carbonyl group with an Oxygen atom next to the carbonyl carbon is indicated.

methyl acetate



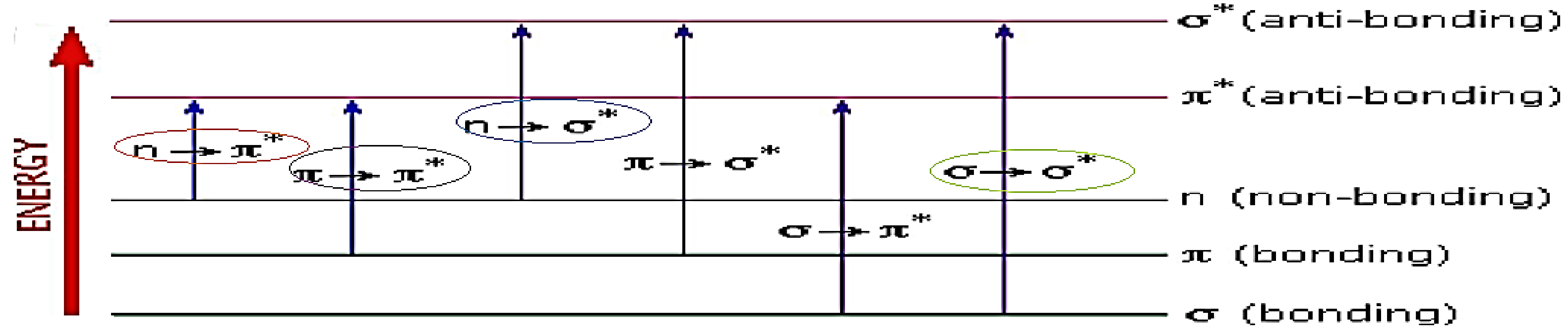
$CH_3-\overset{\overset{O}{\|}}{C}-OCH_3$

Types of Electron Transitions

- The ground state of an organic molecule contains valence electrons in three principal types of molecular orbitals: sigma (σ) orbitals; pi (π) orbitals; and filled but nonbonded orbitals (n).

- Both σ and π orbitals are formed from the overlap of two atomic or hybrid orbitals. Each of these molecular orbitals therefore has an antibonding σ* or π* orbital associated with it.
- An orbital containing *n* electrons does not have an antibonding orbital (because it was not formed from two orbitals).
- Electron transitions involve the promotion of an electron from one of the three ground states (σ, π, or n) to one of the two excited states (σ*, or π*).
- There are six possible transitions; the four important transitions and their relative energies are:

The possible electronic transitions can graphically shown as:



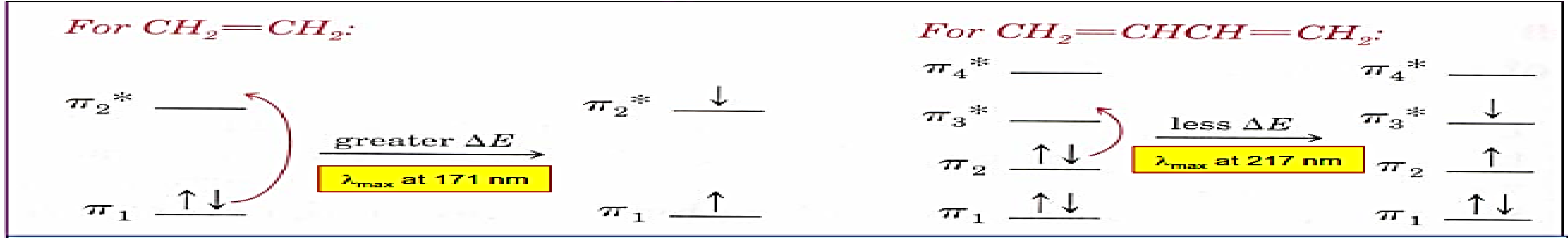
- ☐ The most useful region of the UV spectrum is at wavelengths longer than 200 nm.
- ☐ The following transitions give rise to absorption in the nonuseful 100-200 nm range:
  - $\pi \longrightarrow \pi^*$ for an isolated double bond, and
  - $\sigma \longrightarrow \sigma^*$ for an ordinary carbon-carbon bond.
- ☐ The useful transitions (200 nm-400 nm) are $\pi \longrightarrow \pi^*$ for compounds with conjugated double bonds, and some $n \longrightarrow \sigma^*$ and some $n \longrightarrow \pi^*$ transitions.
- ☐ Alkenes and nonconjugated dienes usually have absorption maxima below 200 nm.

➢ ***Example:***
- Ethene gives an absorption maximum at 171 nm,
- 1,4-pentadiene gives an absorption maximum at 178 nm.

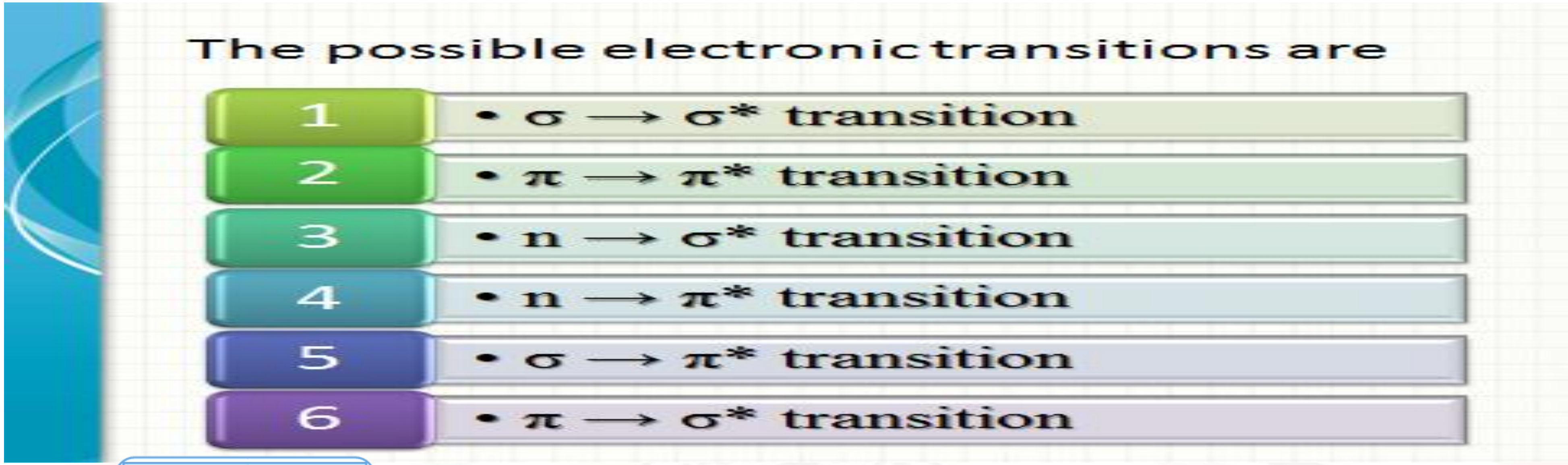
highest occupied molecular orbital (HOMO)
lowest unoccupied molecular orbital(LUMO)

➢ Absorption by Polyenes

- ☐ Compounds whose molecules contain conjugated multiple bonds have absorption maxima at wavelengths longer than 200 nm.
- ☐ For example, less energy is required to promote a π electron of 1,3-butadiene than is needed to promote a π electron of ethylene.
- ☐ The reason is that the energy gap between the HOMO and the LUMO for conjugated double bonds is less than the energy difference for an isolated double bond.
- ☐ Resonance-stabilization of the excited state of a conjugated diene is one factor that decreases the energy of the excited state.



Because less energy is needed for a $\pi \longrightarrow \pi^*$ transition of 1,3-butadiene, this diene absorbs UV radiation of longer wavelengths than does ethylene.



The possible electronic transitions are

1 • $\sigma \longrightarrow \sigma^*$ transition
2 • $\pi \longrightarrow \pi^*$ transition
3 • $n \longrightarrow \sigma^*$ transition
4 • $n \longrightarrow \pi^*$ transition
5 • $\sigma \longrightarrow \pi^*$ transition
6 • $\pi \longrightarrow \sigma^*$ transition

1 • $\sigma \rightarrow \sigma^*$ transition

- σ electron from orbital is excited to corresponding anti-bonding orbital σ*.
- The energy required is large for this transition.
- e.g. Methane (CH_4) has C-H bond only and can undergo $\sigma \rightarrow \sigma^*$ transition and shows absorbance maxima at 125 nm.

Q. The energy required is the highest one for$\sigma \rightarrow \sigma^*$ transition ?

ANS. All saturated alkane need highest energy, so they show shortest wave length, with an exception Cyclopropane because of ring strength which give normal UV region above 200 nm.

2 • π → π* transition

- π electron in a bonding orbital is excited to corresponding anti-bonding orbital π*.
- Compounds containing multiple bonds like alkenes, alkynes, carbonyl, nitriles, aromatic compounds, etc undergo π → π* transitions.
- e.g. Alkenes generally absorb in the region 170 to 205 nm.

3 • n → σ* transition

- Saturated compounds containing atoms with lone pair of electrons like O, N, S and halogens are capable of n → σ* transition.
- These transitions usually requires less energy than σ → σ* transitions.
- The number of organic functional groups with n → σ* peaks in UV region is small (150 – 250 nm).

4 • n → π* transition

- An electron from non-bonding orbital is promoted to anti-bonding π* orbital.
- Compounds containing double bond involving hetero atoms (C=O, C≡N, N=O) undergo such transitions.
- n → π* transitions require minimum energy and show absorption at longer wavelength around 300 nm.

5

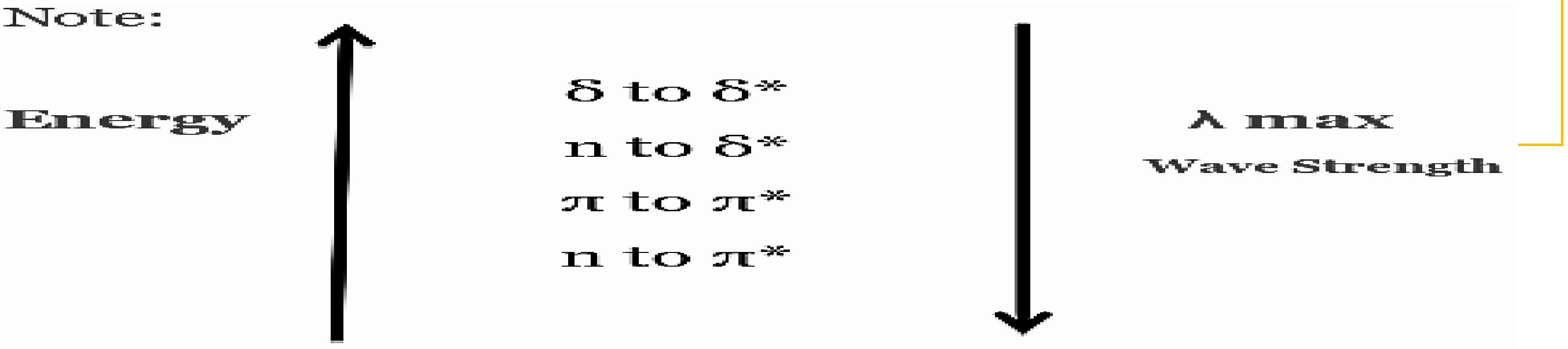
- σ → π* transition

&

- π → σ* transition

6

- These electronic transitions are forbidden transitions & are only theoretically possible.
- Thus, n → π* & π → π* electronic transitions show absorption in region above 200 nm which is accessible to UV-visible spectrophotometer.
- The UV spectrum is of only a few broad of absorption.

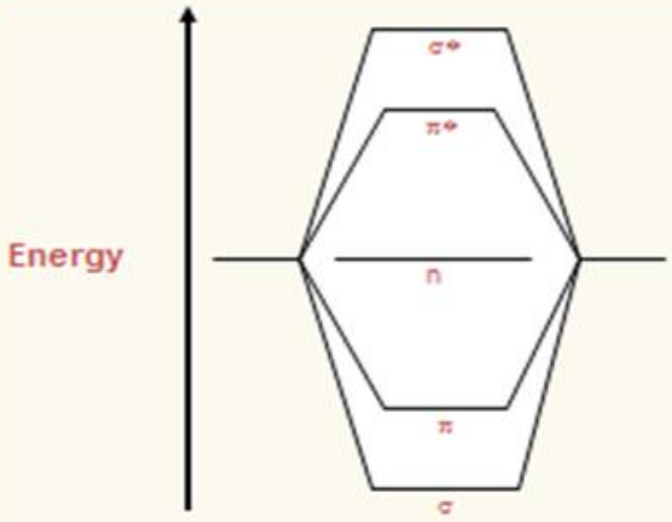


Band Structure

In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states

This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels .

Observed electronic transitions



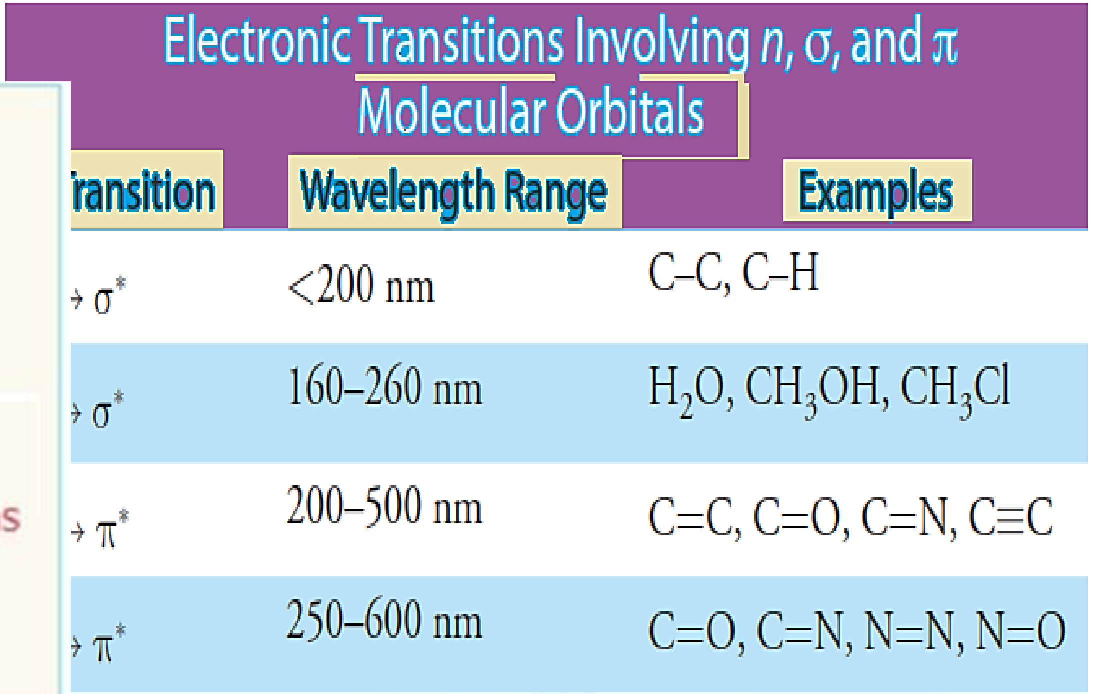
$\sigma \rightarrow \sigma^*$ alkanes

$\sigma \rightarrow \pi^*$ carbonyls

$\pi \rightarrow \pi^*$ unsat cpds.

$n \rightarrow \sigma^*$ O,N,S, halogens

$n \rightarrow \pi^*$ carbonyls



Electronic Transitions Involving *n*, σ, and π Molecular Orbitals

ransition	Wavelength Range	Examples
→ σ^*	<200 nm	C–C, C–H
→ σ^*	160–260 nm	H_2O, CH_3OH, CH_3Cl
→ π^*	200–500 nm	C=C, C=O, C=N, C≡C
→ π^*	250–600 nm	C=O, C=N, N=N, N=O

CH_4 $\sigma \longrightarrow \sigma^*$

$CH_2=CH_2$ $\sigma \longrightarrow \sigma^*$ $\pi \longrightarrow \pi^*$

CH_3-(R) C=O 1- $\sigma \longrightarrow \sigma^*$ 2- $\pi \longrightarrow \pi^*$
3- $n \longrightarrow \sigma^*$ 4- $n \longrightarrow \pi^*$

CH_2=CH-OH
As the above example (1-4)

CH_2=CH-CH_2-OH
As the above example (1-3) no 4 x

π−π∗ Transition is the most convenient and useful transition in UV-Vis Spectroscopy. Why?

In σ−σ* transitions :

- The high energy required can cause rupture of the s bonds and breakdown of the molecule.
- Air components absorb in vacuum UV which limits the application of the method ,working in vacuum UV requires special training
- Special sources and detectors.
- All solvents contain σ bonds

In n-σ* transitions :

- The absorption wavelength for a n-σ * transition occurs at about 185 nm where, unfortunately, most solvents absorb. For example, water which has two pairs of nonbonding electrons that will strongly absorb as a result of the n-σ * .(H2O and other solvents with nonbonding electrons).
- in polar solvents the energy required for the n-σ* increases and thus the probability for the transition decreases.

In n-π* transitions :

- requires very little energy , However, unfortunately, the absorptivity of this transition is very small which precludes its use for sensitive quantitative analysis.
- using polar solvents increases the energy required for this transition, thus decreasing its probability.

In π−π* transitions : The most frequently used transition is the π−π* transition for the following reasons:

- The molar absorptivity for the π−π* transition is high allowing sensitive determinations.
- The energy required is moderate, far less than dissociation energy.
- In presence of the most convenient solvent (water), the energy required for a π−π* transition is usually smaller.

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

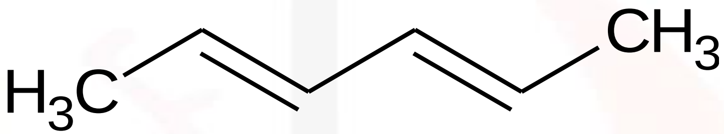
To interpretate UV – visible spectrum following points should be noted:

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.

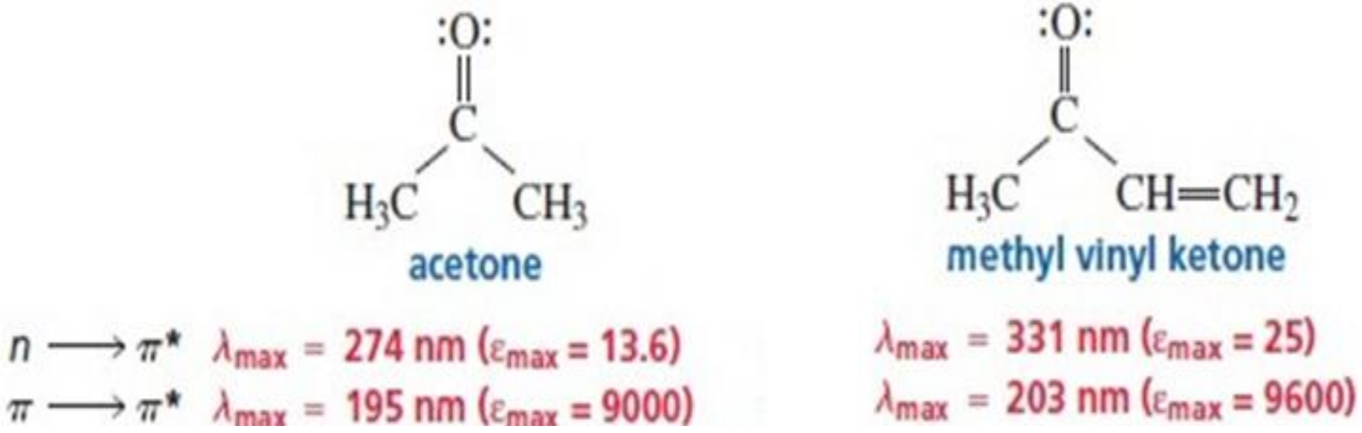
e.g. 1,5 - hexadiene has λ_{max} = 178 nm 2,4 - hexadiene has λ_{max} = 227 nm



Effect of Conjugation on λ_{max}

The n→π* transition for methyl vinyl ketone is at 331 nm, and the π→π* transition is at 203 nm. Both λ_{max} values are at longer wavelengths than the corresponding λ_{max} values of acetone because methyl vinyl ketone has two conjugated double bonds.

“The λ_{max} increases as the number of conjugated double bonds increases.”



$n \longrightarrow \pi^*$ λ_{max} = 274 nm (ε_{max} = 13.6)
$\pi \longrightarrow \pi^*$ λ_{max} = 195 nm (ε_{max} = 9000)

λ_{max} = 331 nm (ε_{max} = 25)
λ_{max} = 203 nm (ε_{max} = 9600)

The more conjugated double bonds there are in a compound, the less energy is required for the electronic transition, and therefore the longer is the wavelength at which the electronic transition occurs.

Auxochrome

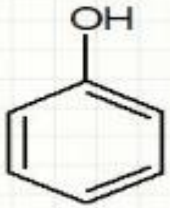
The functional groups attached to a chromophore which modifies the ability of the chromophore to absorb light , altering the wavelength or intensity of absorption.

OR

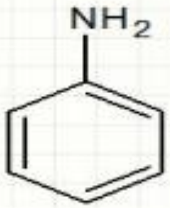
The functional group with non-bonding electrons that does not absorb radiation in near UV region but when attached to a chromophore alters the wavelength & intensity of absorption.

e.g. Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm



Aniline λ_{max} = 280 nm



➡ **Bathochromic Shift (Red Shift)**

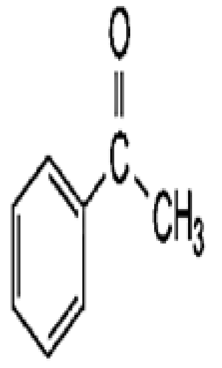
If the group attached to the ring bears *n* electrons, they can induce a shift in the primary and secondary absorption bands

Increase λmax. Of E1 (not appear)
E2 (shorter to appear)
& B with increase E max.
Or stable and loss its fine structure

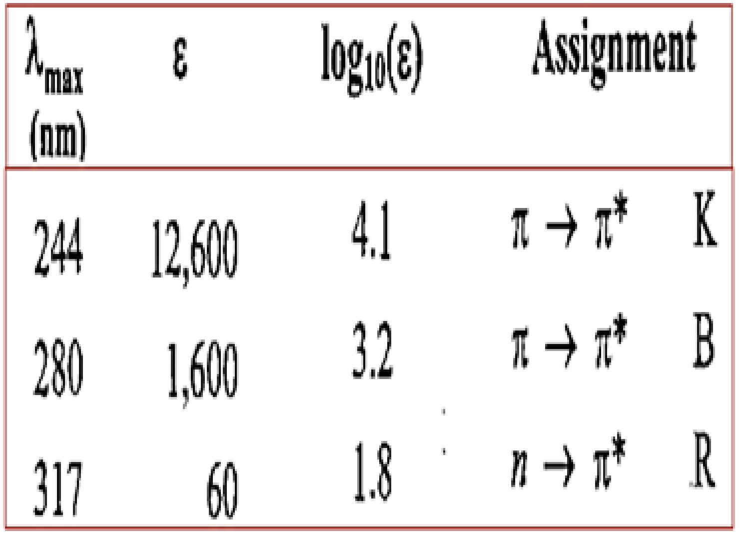
Another method of classification uses the symbols:

B	(for benzenoid)	R	(for radical-like)
E	(for ethylenic)	K	(for conjugated)

A molecule may give rise to more than one band in its UV spectrum, either because it contains more than one chromophore or because more than one transition of a single chromophore is observed.



acetophenone



λ_{max} (nm)	ε	$\log_{10}(\varepsilon)$	Assignment	
244	12,600	4.1	$\pi \rightarrow \pi^*$	K
280	1,600	3.2	$\pi \rightarrow \pi^*$	B
317	60	1.8	$n \rightarrow \pi^*$	R

B band (Benzene band, Benzenoid bands) from the π → π* transition of Benzene. Broad band with fine structure between 230 – 270 nm. This band can be used to identify aromatic compound.

E band (Ethylenic bands) also from π → π* transition of ethylenic band in benzene
E1 band and E2 band

R band originated from *n* - π* transition transition.
The maximum absorption wavelength > 270 nm, $\epsilon_{max} < 100$
Example: Acetone λ_{max} 279 nm, $\epsilon_{max} = 15$

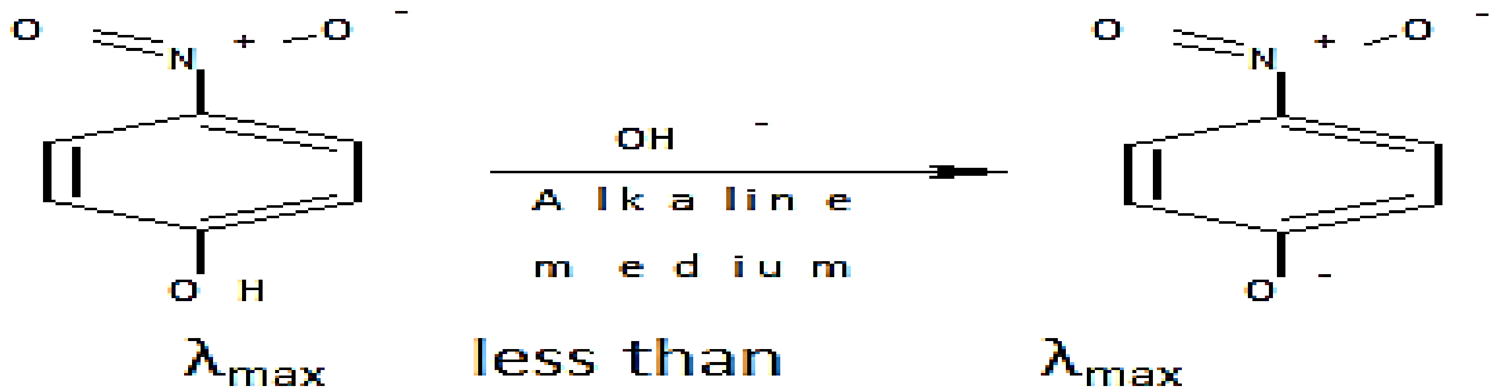
K band (conjugation band, form π → π* transition.
High ϵ_{max} ($> 10^4$)
Example: Dienes , Acetophenone

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.

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

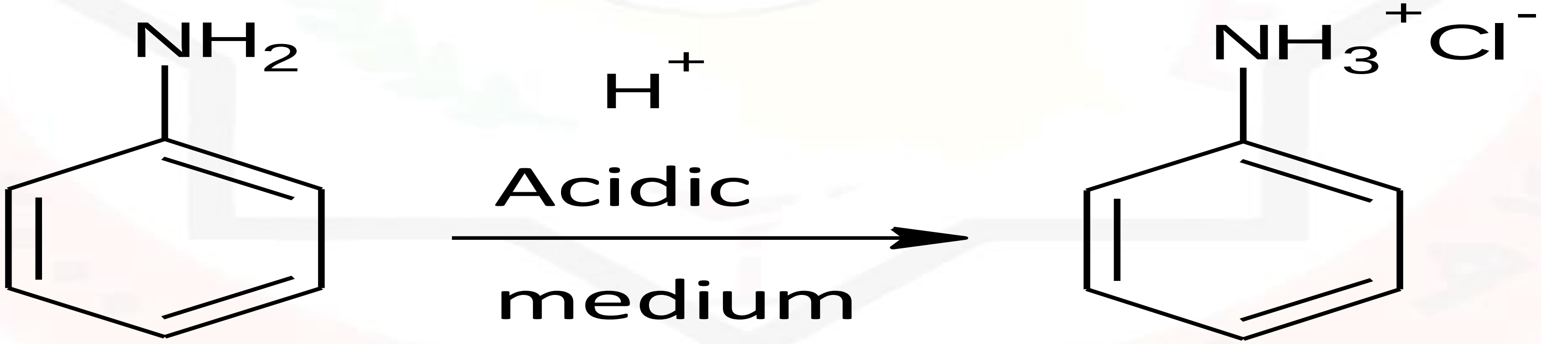


2 • Hypsochromic Shift (Blue Shift)

- 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.

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



Aniline

λ_{max} = 280 nm

λ_{max} = 265 nm

3

Hyperchromic Effect

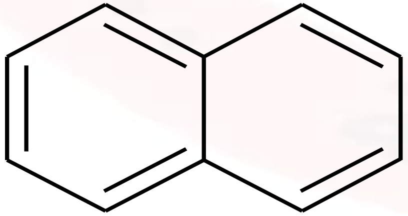
- When absorption intensity (ε) of a compound is increased, it is known as hyperchromic shift.

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

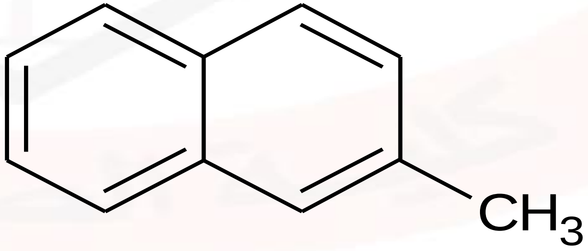
4

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

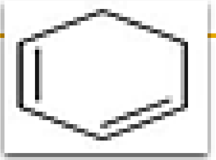
Woodward – Fieser’s rules for calculating λ_{max}

BASIC INTRODUCTION:-

The central bond is a part of the ring system, the diene chromophore is usually held rigidly in either the s-*trans* or the s-*cis* conformation

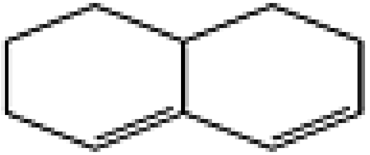
- HOMOANNULAR:- cyclic diene having conjugated double bonds in same ring.

  (s-cis) cyclic dienes having conjugated double bonds in the same ring. e.g.

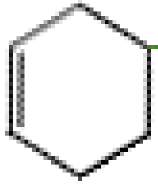


- HETEROANNULAR:-cyclic diene having conjugated double bonds in different rings

  (s-trans) cyclic dienes having Conjugated double bonds not in the same ring. e.g

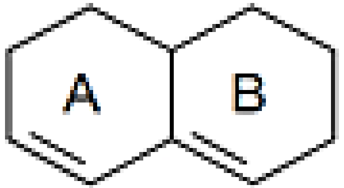


ENDOCYCLIC DOUBLE BOND:-double bond present in a ring.

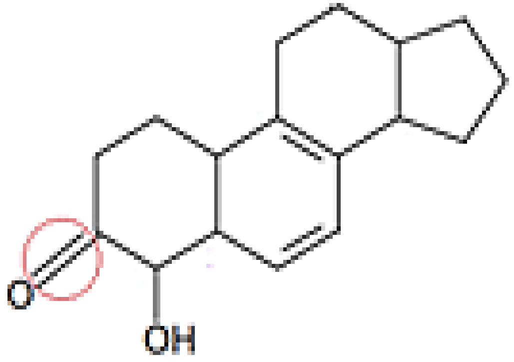


EXOCYCLIC DOUBLE BOND:-double bond in which one of the doubly atoms is a part of ring system.ring A has only one endocyclic double bond

ring B has one exocyclic and endocyclic double bond .



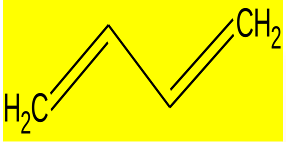
Double bond extending :- When more double bonds are present other than conjugations.



Different Terms

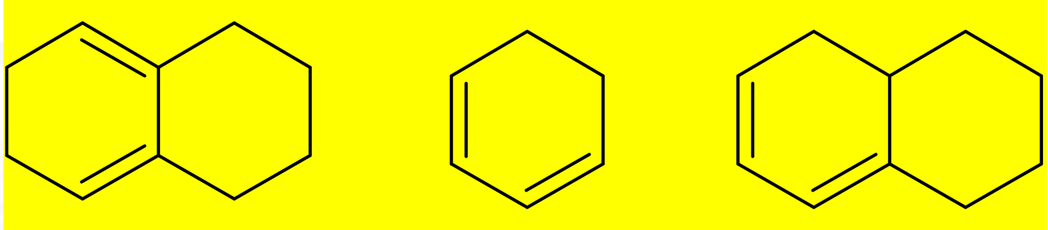
1. **Alicylic dienes or dienes contained in an open chain system**

i.e, where basic unit is butadiene system.



2. Homoannular conjugated double bonds

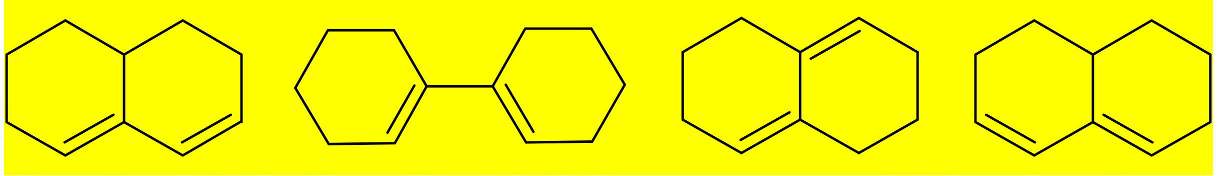
Are the conjugated double bond present in the same ring. it is also called as Homodiene. some examples of this type are:



Different Terms

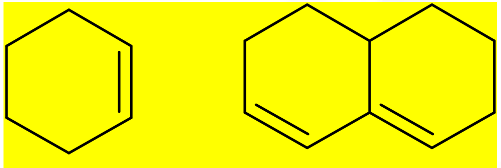
3. Heteroannular conjugated double bonds

Are the double bonds which are present in different ring. for example.



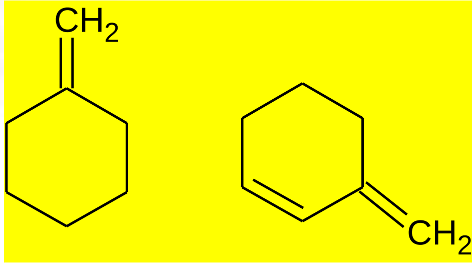
4. Endocyclic double bond

The double bond present in a ring only (inside).



5. Exocyclic double bond

The double bond is a part of the ring (outside).



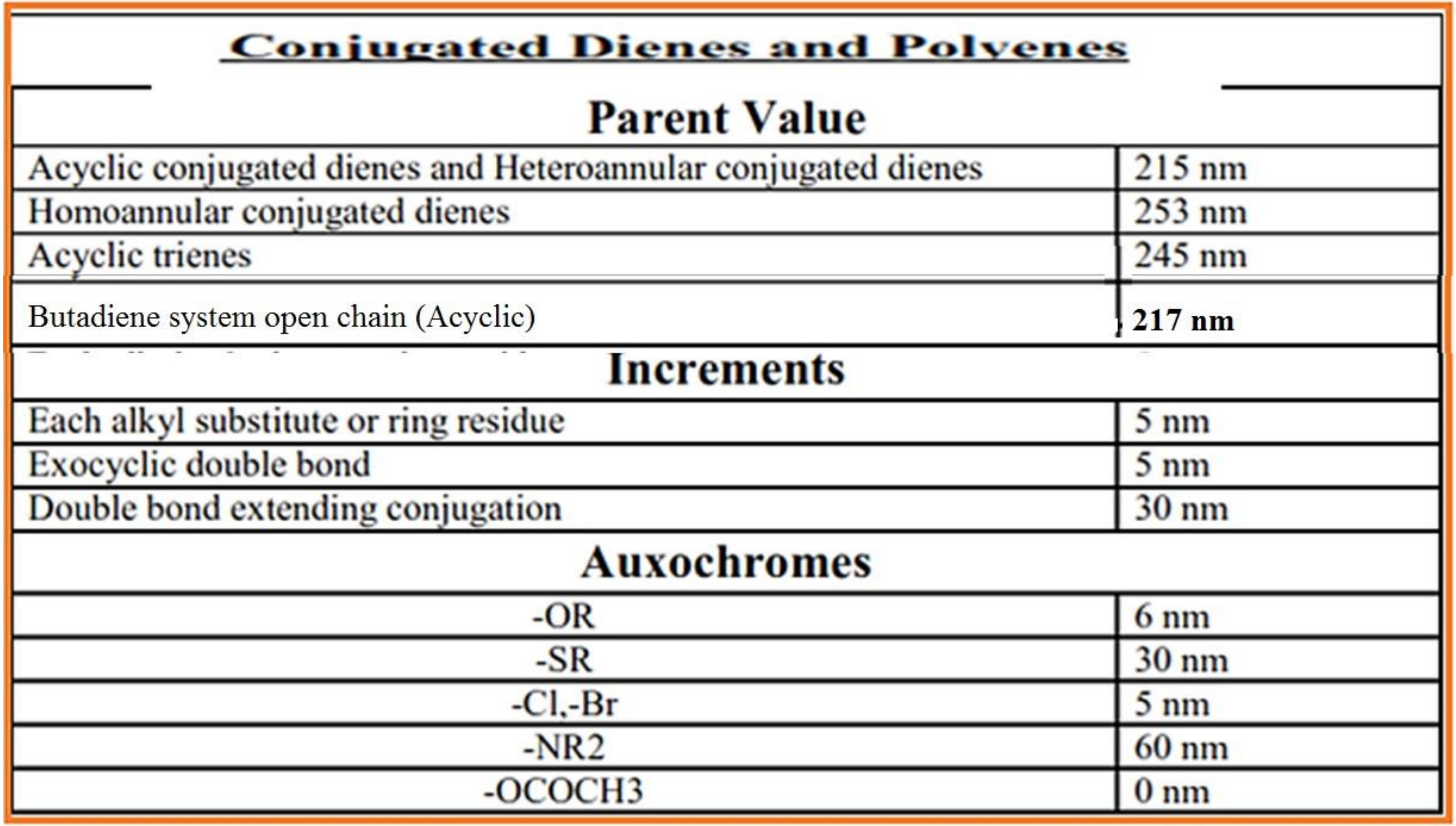
Woodward – Fieser's rules for conjugated dienes, trienes, polyenes etc

- According to this rules each type of dienes or trienes system is having a certain fixed value at which absorption takes place.

- This constitutes the ***basic value*** or ***parent value***.

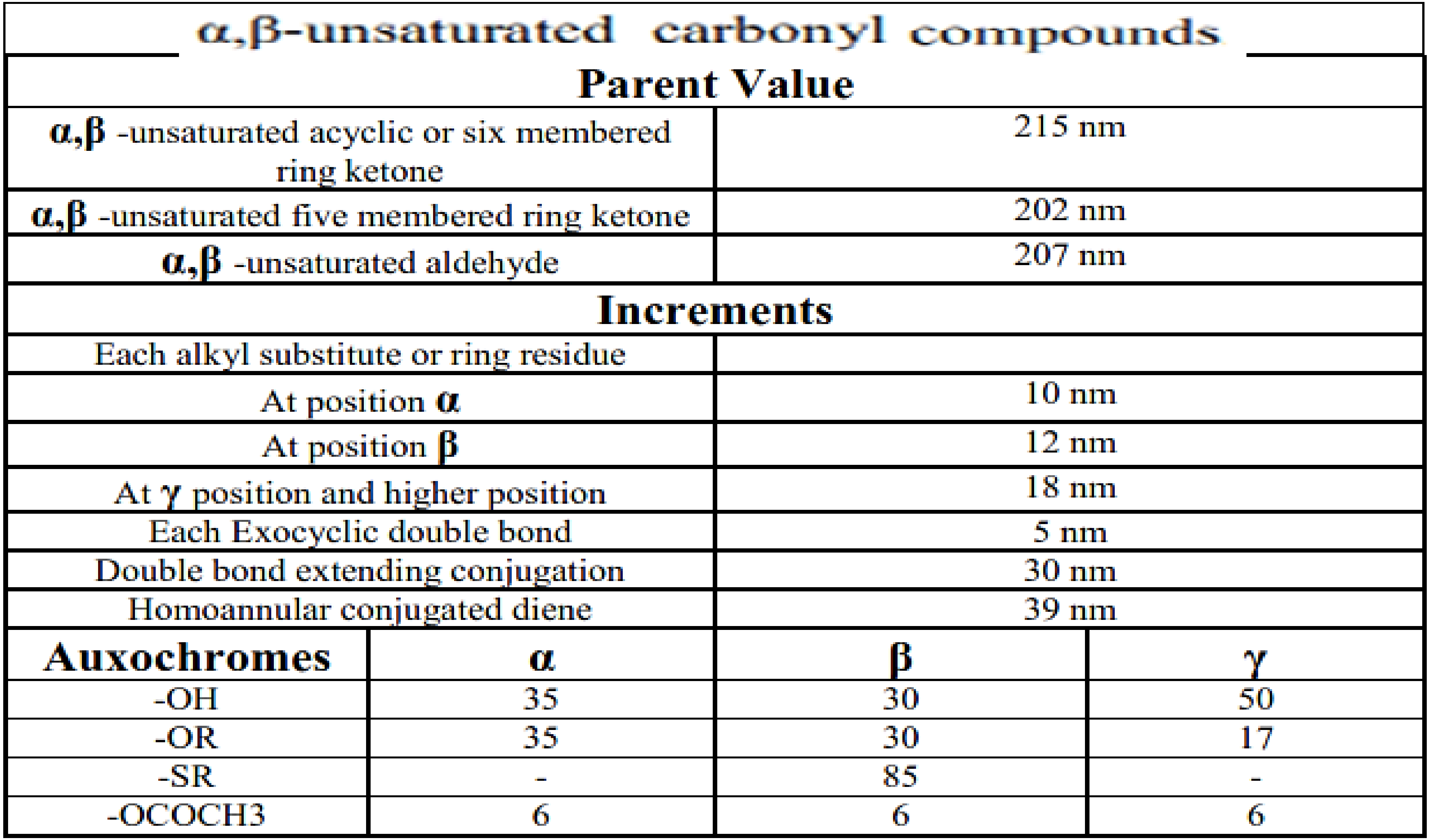
This value of absorption maximum depends upon:-

- ✓The number of alkyl substitution or ring residues
- ✓The number of double bonds which extending conjugation
- ✓The presence of polar groups such as Cl, Br, OR, are added to the basic value to obtain $\boldsymbol{\lambda}_{max}$ for a particular compound.



Conjugated Dienes and Polyenes

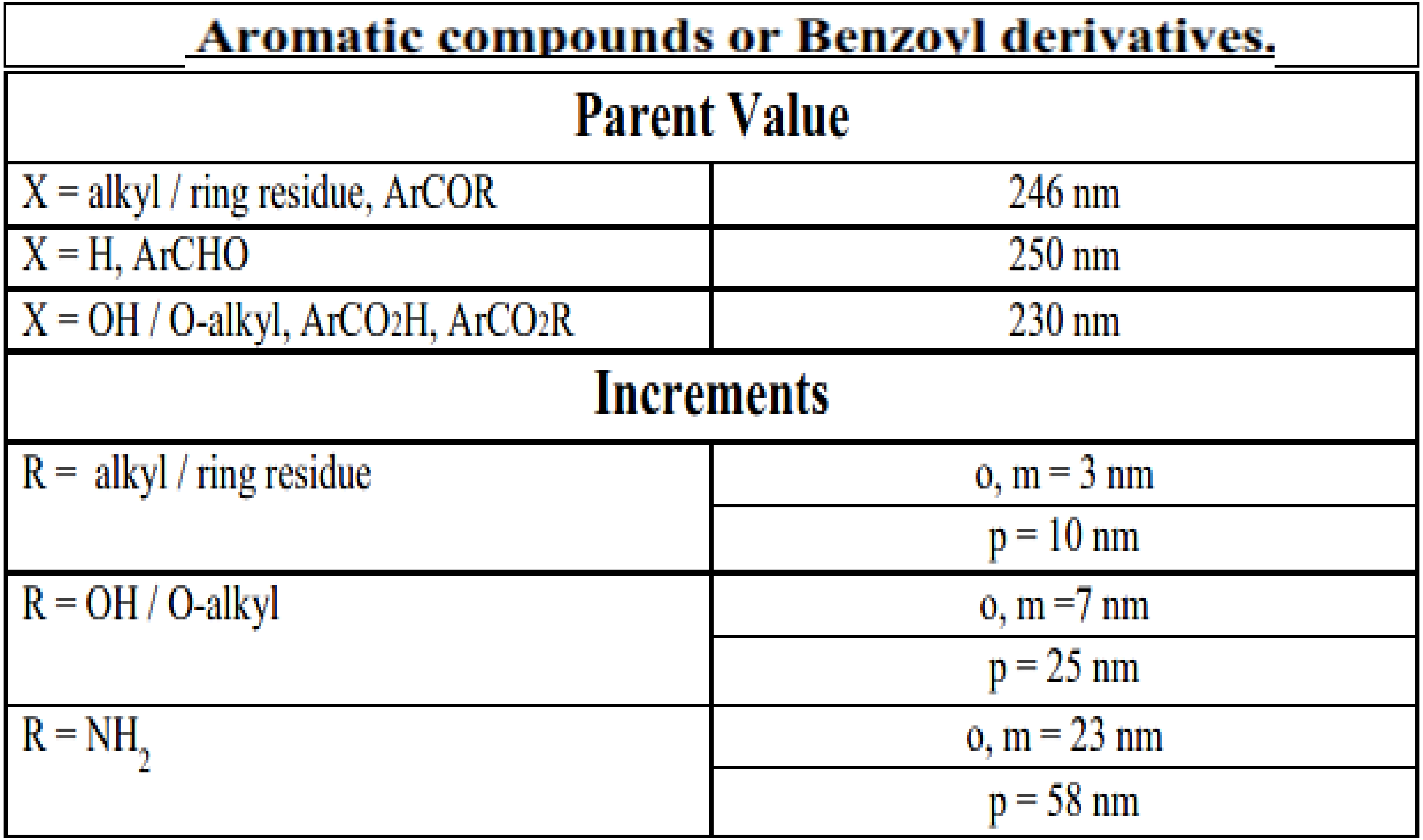
Parent Value	
Acyclic conjugated dienes and Heteroannular conjugated dienes	215 nm
Homoannular conjugated dienes	253 nm
Acyclic trienes	245 nm
Butadiene system open chain (Acyclic)	**217 nm**
Increments	
Each alkyl substitute or ring residue	5 nm
Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Auxochromes	
-OR	6 nm
-SR	30 nm
-Cl,-Br	5 nm
-NR2	60 nm
-OCOCH3	0 nm



α,β-unsaturated carbonyl compounds

Parent Value	
α,β -unsaturated acyclic or six membered ring ketone	215 nm
α,β -unsaturated five membered ring ketone	202 nm
α,β -unsaturated aldehyde	207 nm
Increments	
Each alkyl substitute or ring residue	
At position **α**	10 nm
At position **β**	12 nm
At γ position and higher position	18 nm
Each Exocyclic double bond	5 nm
Double bond extending conjugation	30 nm
Homoannular conjugated diene	39 nm

Auxochromes	**α**	**β**	**γ**
-OH	35	30	50
-OR	35	30	17
-SR	-	85	-
-OCOCH3	6	6	6

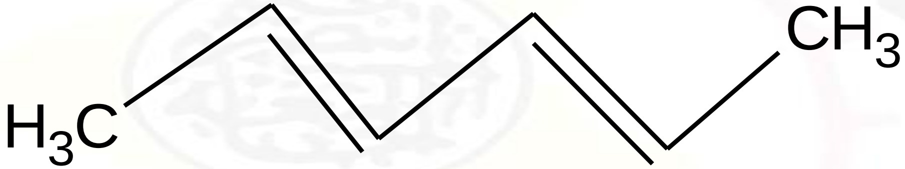


Aromatic compounds or Benzoyl derivatives.

Parent Value	
X = alkyl / ring residue, ArCOR	246 nm
X = H, ArCHO	250 nm
X = OH / O-alkyl, $ArCO_2H$, $ArCO_2R$	230 nm
Increments	
R = alkyl / ring residue	o, m = 3 nm
	p = 10 nm
R = OH / O-alkyl	o, m =7 nm
	p = 25 nm
R = NH_2	o, m = 23 nm
	p = 58 nm

EXAMPLES

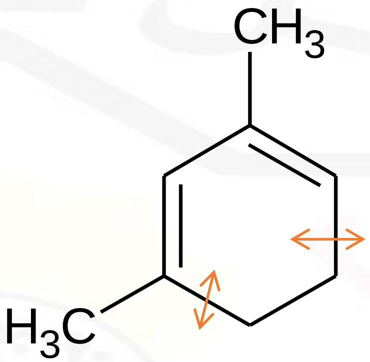
1. Calculate absorption maximum in UV Spectrum of 2,4 Hexadiene.



- Butadiene system; basic value = 217nm
- 2 Alkyl substituent(2X5nm) = 10nm

- Calculated value = 227 nm
- Observed value = 227 nm

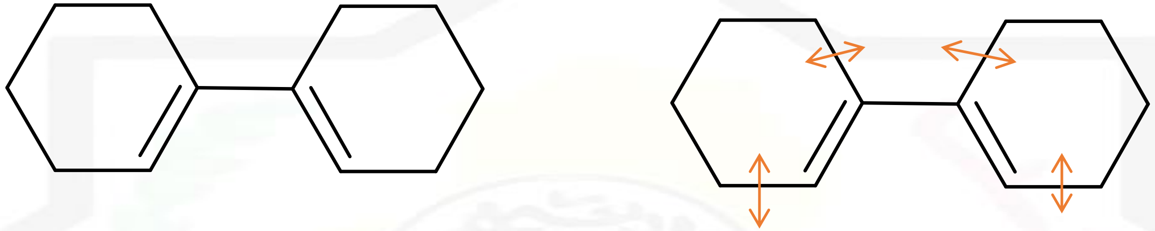
2. Calculate λ max for 1,4- dimethylcyclohex-1,3-diene



- Parent value for homoannular ring : = 253 nm
- Two alkyl substituents : 2 x 5 = 10 nm

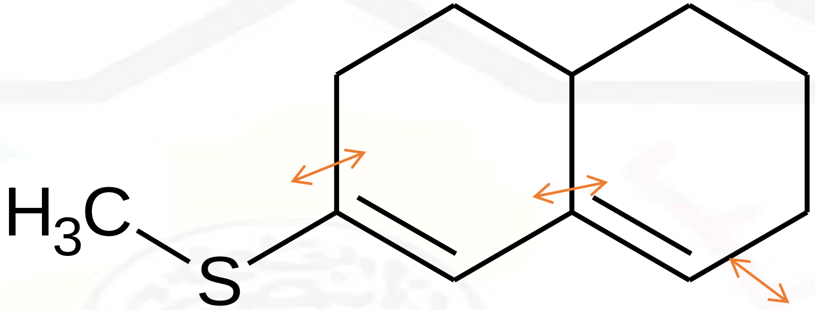
- calculated value : = 273 nm
- observed value : = 263 nm

3. Calculate λ max of following compound



- Parent value for heteroannular diene : = 214 nm
- Four ring residue : 4 X5 = 20 nm

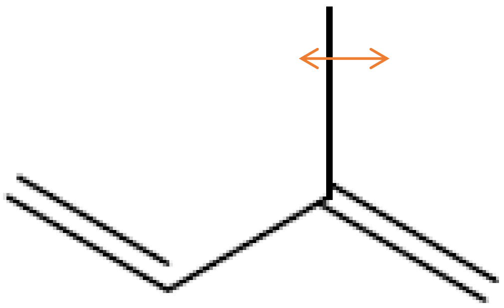
- Calculated value : = 234 nm
- Observed value : = 236 nm



- Parent value for heteroannular diene : = 214 nm
- 3 ring residue : 3 X5 = 15 nm
- Exocyclic double bond = 5 nm
- Thiomethyl substituent =30 nm

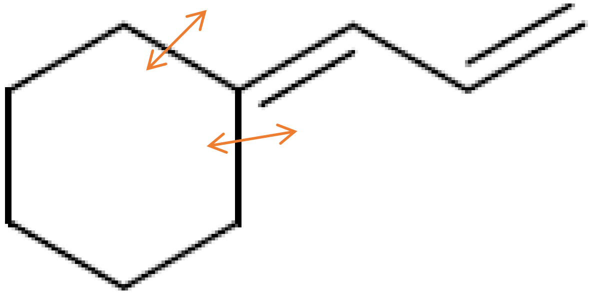
- Calculated value : = 264 nm
- Observed value : = 268 nm

Isoprene - acyclic butadiene =	217 nm

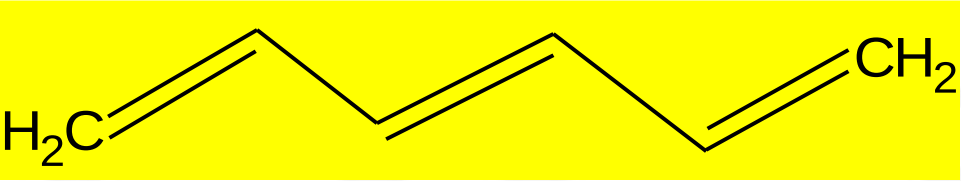


one alkyl subs.	+ 5 nm
Calculated value	222 nm
Observed value	220 nm

Allylidenecyclohexane - acyclic butadiene =	217 nm



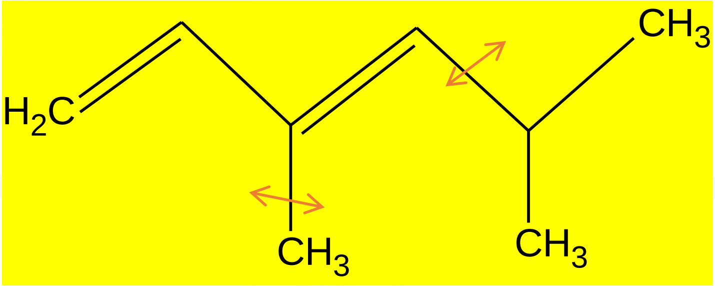
one exocyclic C=C	+ 5 nm
2 alkyl subs.	+10 nm
Calculated value	232 nm
Observed value	237 nm



Acyclic butadiene = 217 nm

Extended conjugation = +30 nm

Calculated value = 247 nm

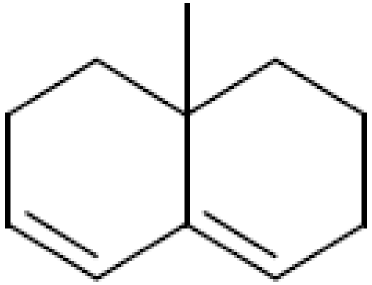


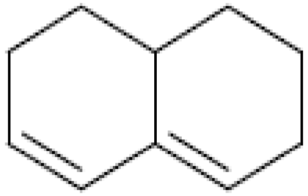
Acyclic base = 217 nm

2 alkyl substitution = 10 nm

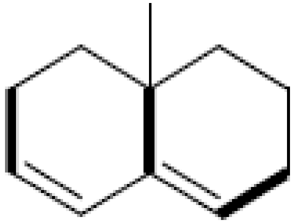
Calculated value = 227 nm

1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene

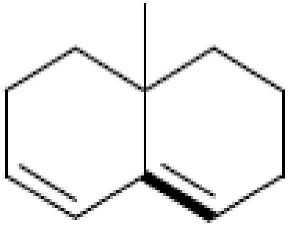




Heteroannular diene = 214 nm



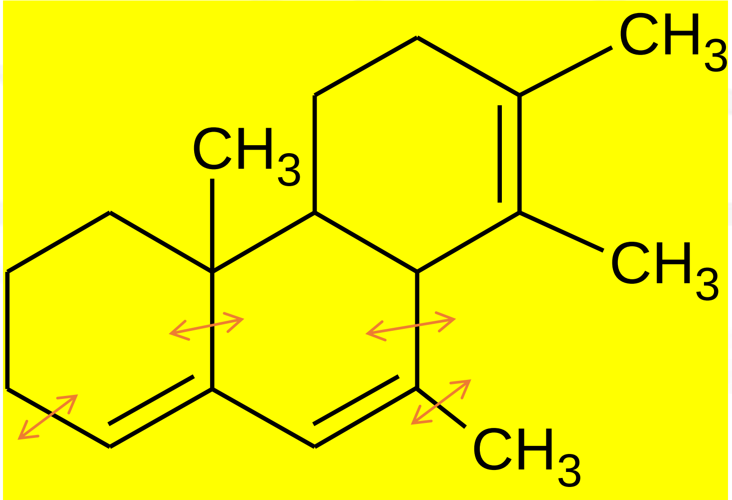
3 alkyl subs. (3 x 5) = +15 nm



1 exo C=C = + 5 nm

Calculated value 234 nm

Observed value 235 nm



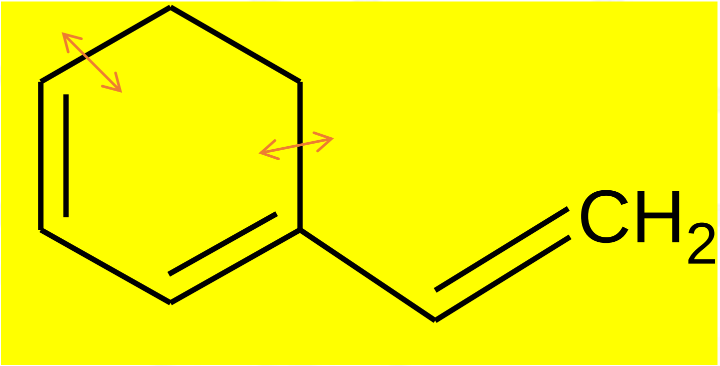
Parent value for heteroannular : = 214 nm

Four ring residue : 4 X5 = 20 nm

Exocyclic double bond =5 nm

Calculated value : = 239 nm

Observed value : = 236 nm

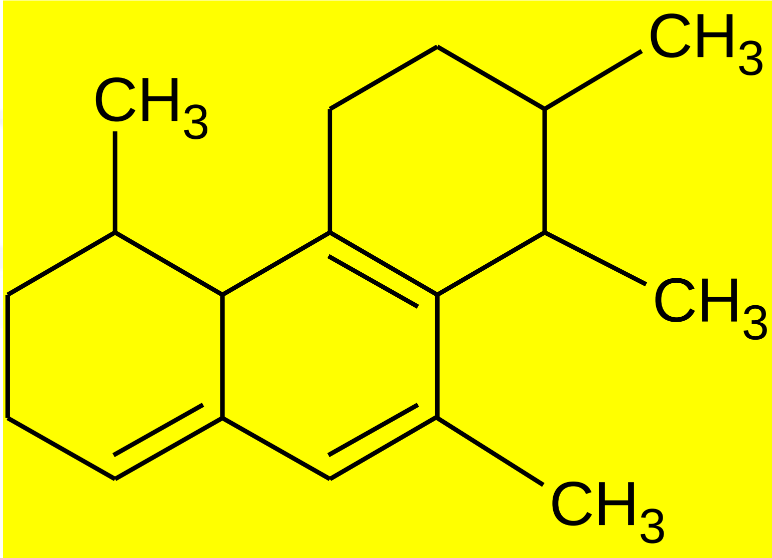


Parent value for homoannular : = 253 nm

Extended conjugation 1 X30 = 30 nm

Alkyl substitution 2x5 =10 nm

Calculated value : = 293 nm



Parent value for homoannular (the highest value) : = 253 nm

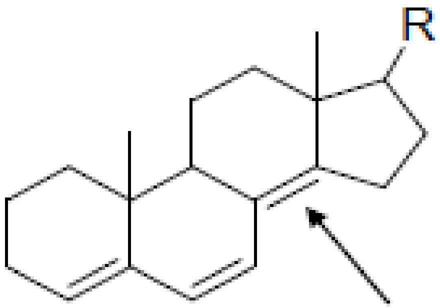
Extended conjugation 1 X30 = 30 nm

Exocyclic double bond =5 nm

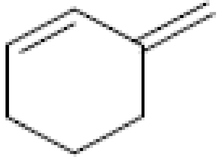
Alkyl substitution or ring residue 6x5 =30 nm

Calculated value : = 318 nm

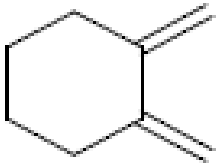
Be careful with your assignments – three common errors:



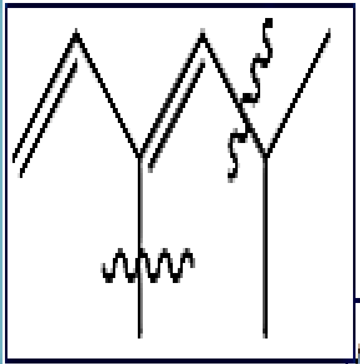
This compound has three exocyclic double bonds; the indicated bond is exocyclic to ***two*** rings



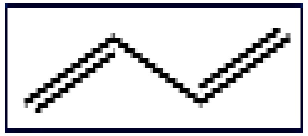
This is ***not*** a heteroannular diene; you would use the base value for an acyclic diene



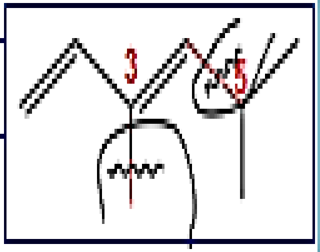
Likewise, this is ***not*** a homooannular diene; you would use the base value for an acyclic diene



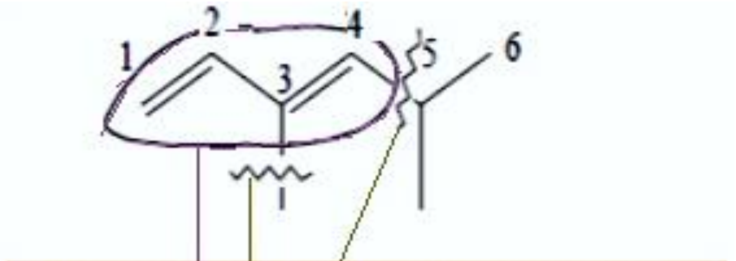
Parent value for Acyclic conjugated diene = 215 nm



Alkyl Substitute or Ring residue at C-3 and C-5 = 5+5= 10 nm

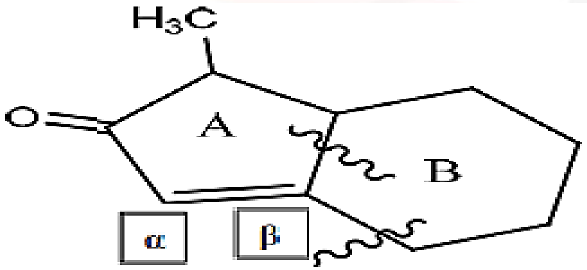


So, λ_{max} would be = (215+10) nm = 225 nm   Observed value = 225 + - 5 nm



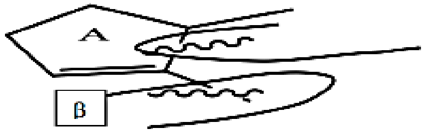
One way to identify an auxochrome is :

- draw a loop around the entire conjugated system (including extending olefins)
- then add hash marks across all bonds attached to the loop. The hash marks define auxochrome attachments.



Parent value for **α, β** unsaturated 5 membered enone = 202 nm

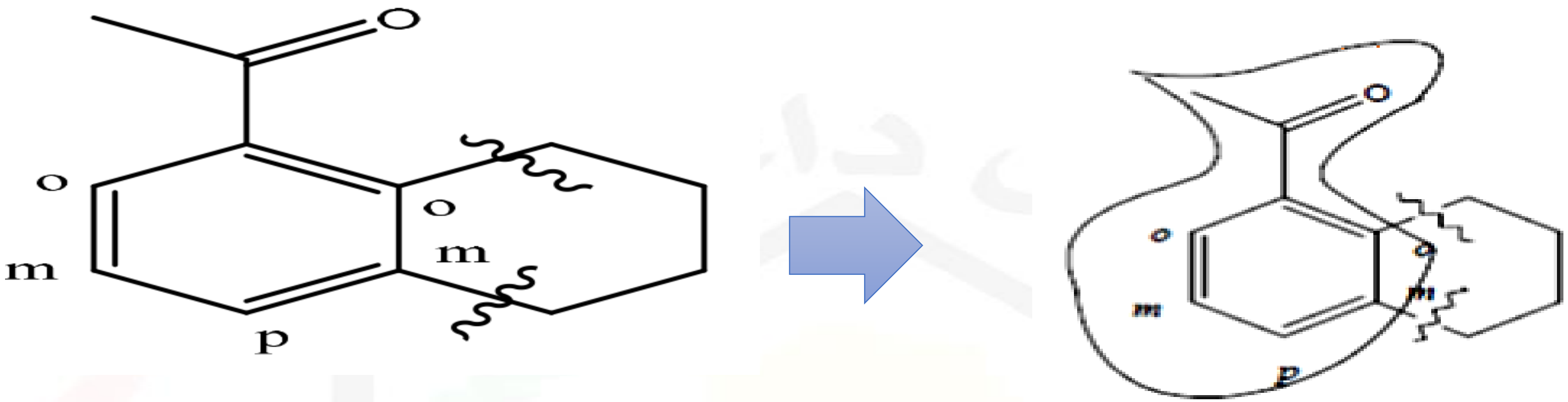
β ring residue = (12 x 2) nm = 24 nm



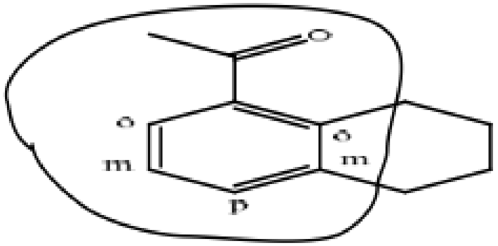
Exocyclic double bond (in respect of ring B) = 5 nm

So, λ_{max} would be = (202+24+5) nm = 231 nm

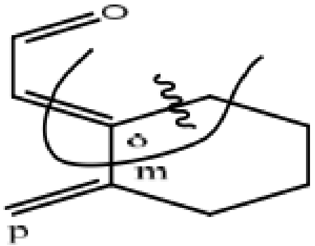
Observed value would be = 231 + - 5 nm



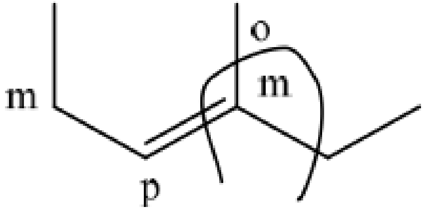
Parent value for Benzoyl group (aliphatic methyl group) = 246 nm



Auxochrome at Ortho Position = 3 nm

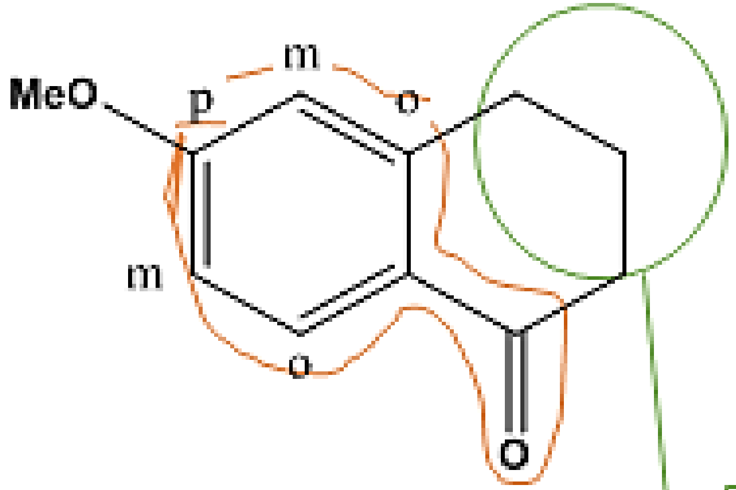


Auxochrome at Meta position = 3 nm



So, λ_{max} would be = (246+3+3) nm = 252 nm

Observed value would be = 252 + - 5 nm



Ketone

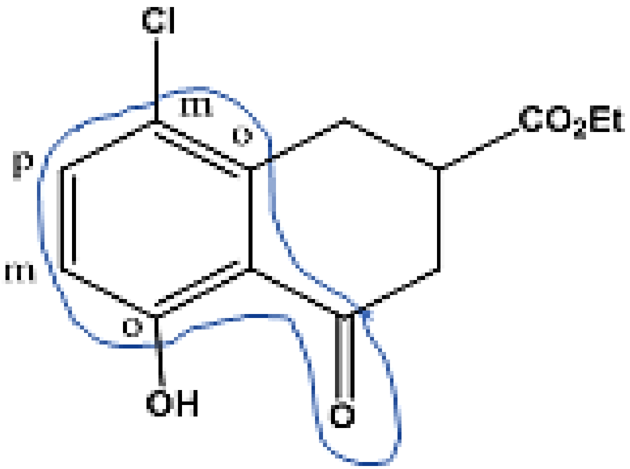
λmax.

Parent comp.	246
Ring residue	+3
P-OCH3	+25

λmax. EtOH

calc. 274 nm

Obs. 276nm



Ketone

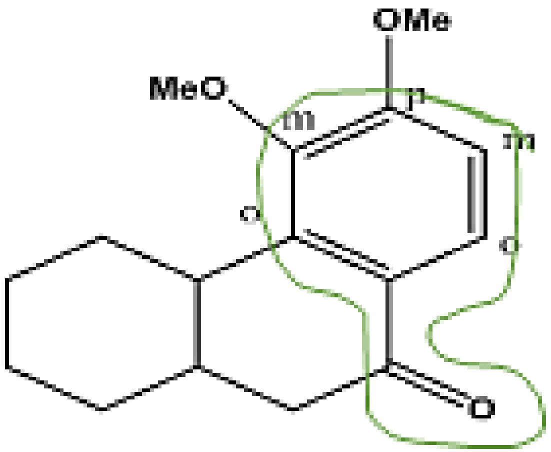
λmax.

Parent comp.	246
Ring residue	+3
O-OH	+7
m- Cl	+0

λmax. EtOH

calc. 256 nm

Obs. 257nm



Ketone

λmax.

Parent comp.	246
Ring residue	+3
P-OCH3	+25
m- OCH3	+7

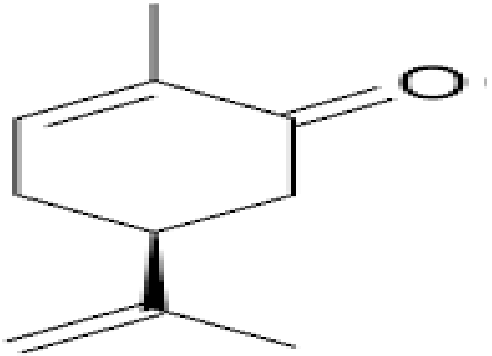
λmax. EtOH

calc. 281 nm

Obs. 278nm

Calculate the λmax for the following compounds :

①



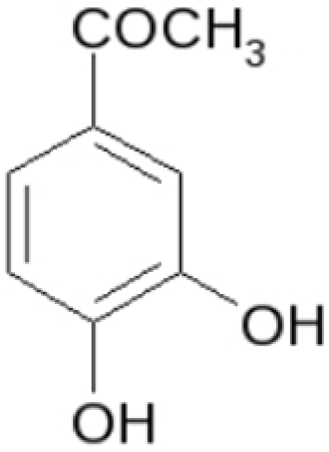
Parent conjugated enone in six membered ring = 215 nm

Substitution of alkyl groups at α position = 10 nm

Substitution of alkyl residue at β position = 12 nm

λ_{max} = **237 nm**

②



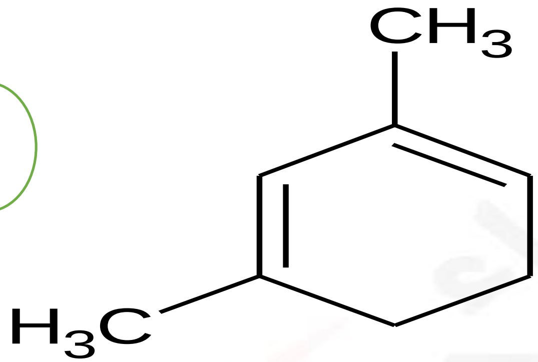
base value = 246 nm

Hydroxy group at meta position = 07 nm

Hydroxy group at para position = 25 nm

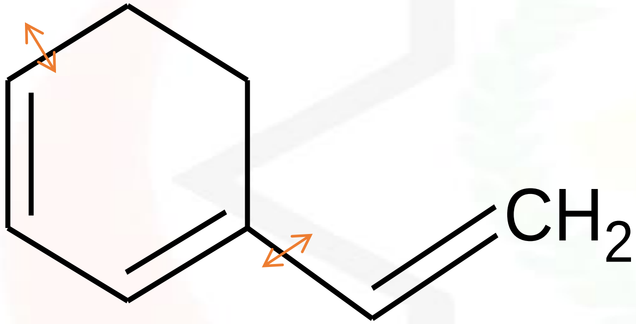
λ_{max} = 278 nm

③



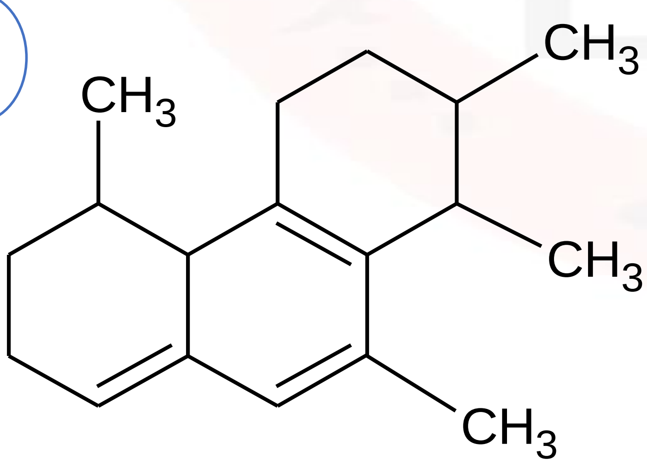
- Parent value for homoannular ring := 253 nm
- Two alkyl substituents : 2 x 5 = 10 nm
- Two ring residue : 2 x 5 = 10 nm
- calculated value : = 273 nm
- observed value : = 263 nm

④

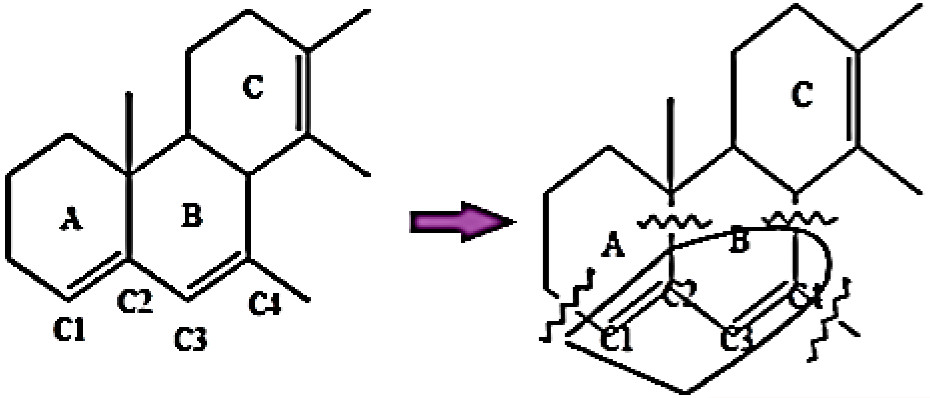


Parent value for homoannular :		= 253 nm
Extended conjugation	1 X30	= 30 nm
Alkyl substitution	2x5	=10 nm
Calculated value :		= 293 nm

⑤



Parent value for homoannular (the highest value)		= 253 nm
Extended conjugation	1 X30	= 30 nm
Exocyclic double bond		=5 nm
Alkyl substitution or ring residue	6x5	=30 nm
Calculated value :		= 318 nm



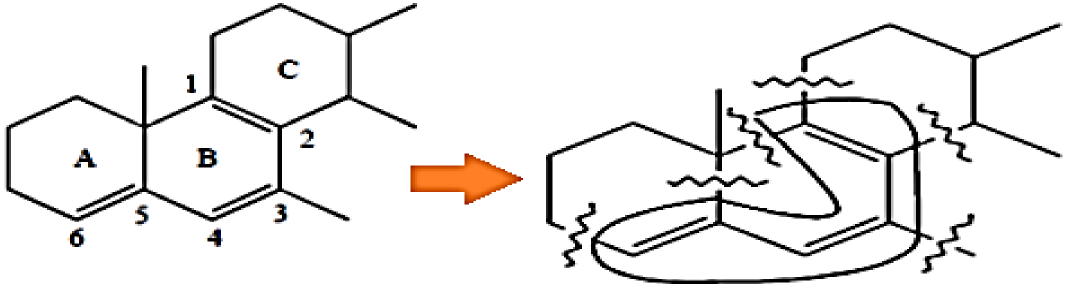
Calc. λ_{max} =

215 (heteroannular since two pi bonds are not in the same ring)

+20 (5 + 5 + 5 + 5 = 20, for each of the alkyl or ring auxochromes attached to C_1, C_3, C_4, and C_4)

+5 (pi bond of C_1-C_2 is exocyclic to ring B)

=240 nm



Calc. λ_{max} =

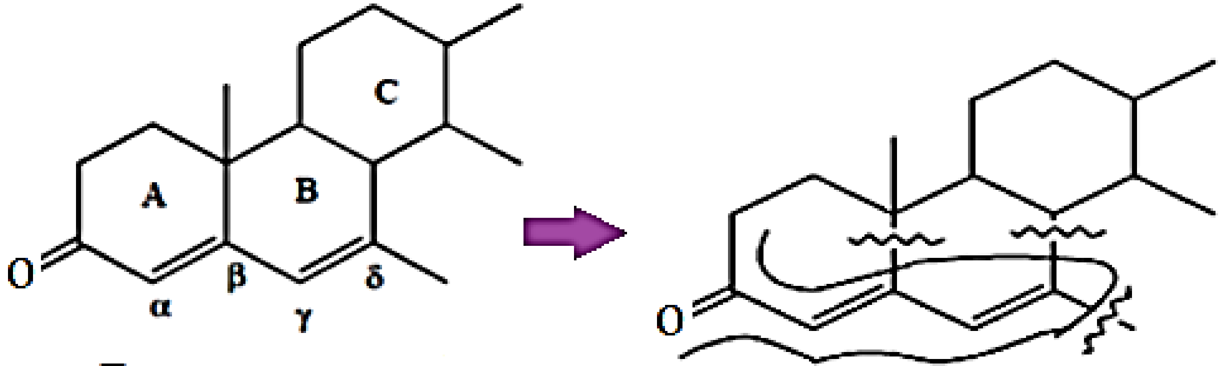
253 (choose diene with highest base value, pi bonds $C_{1\text{-}2}$ and $C_{3\text{-}4}$ are within same ring, so homoannular base should be selected)

+ 30 ($C_{5\text{-}6}$ pi bond is conjugated to diene and is therefore an extending diene)

+ 5 ($C_{5\text{-}6}$ is exocyclic to ring B)

+ 30 (5 + 5 + 5 + 5 + 5 + 5 = 30, for the alkyl or ring auxochromes at C_1, C_1, C_2, C_3, C_5, and C_6)

= 318 nm



Enone

Calc. λ_{max} :

215 (cyclohexenone base)

+ 30 (extending conjugation)

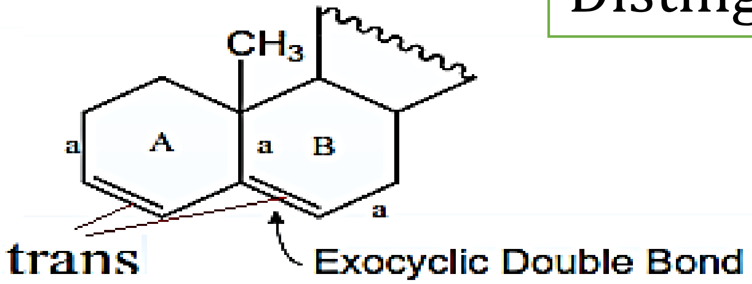
+ 5 (α,β olefin is exocyclic to ring B)

+ 12 (β auxochrome)

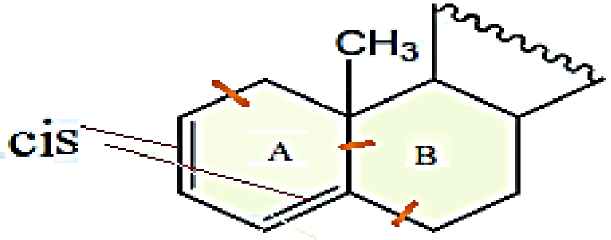
+ 36 (2 δ auxochromes)

= 298 nm

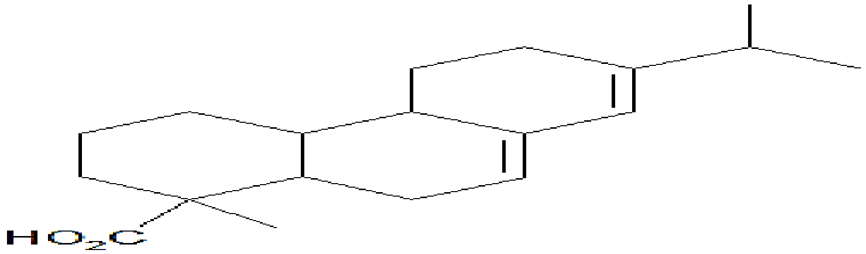
Distinguish Isomers



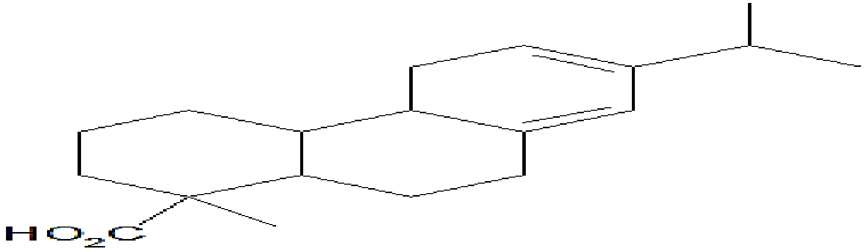
heteroannular or open diene	214 nm
ring residues: 3 × 5 =	15
exocyclic double bond:	5
	234 nm
observed:	235 nm



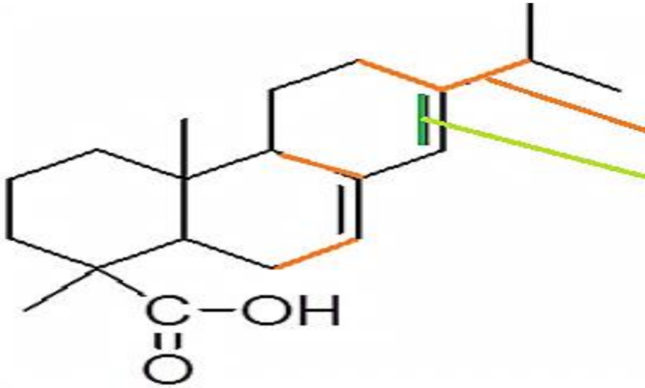
homoannular diene	253 nm
ring residues: 3 × 5 =	15
exocyclic double bond:	5
	273 nm
observed:	275 nm



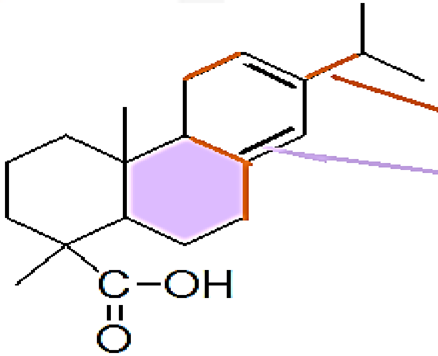
Base value	214
4 x alkyl subst.	20
exo DB	5
total	239
Obs.	238



Base value	253
4 x alkyl subst.	20
total	273
Obs.	273

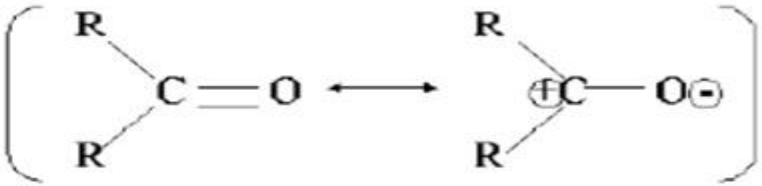


heteroannular diene =	214 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
239 nm	



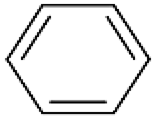
homoannular diene =	253 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
278 nm	

The structure of aldehydes and ketones has been studied and they were shown:



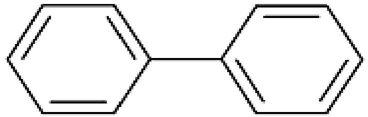
The position of absorption that involves nonbonding electrons n to δ and n to π is particularly sensitive to polarity of the solvent used.

How do you explain the fact that λ_{max} for compounds **I** and **II** are vastly different whereas those of **III** and **IV** are very similar?



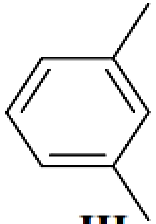
I

204 nm



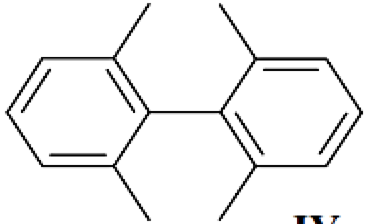
II

246 nm



III

211 nm



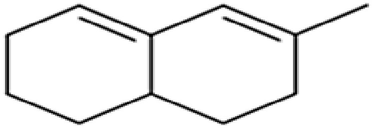
IV

218 nm

I and II: II more or less planar, extended conjugation over both rings

III and IV: IV considerably twisted, conjugation only over one ring as in III;IV is just twice III

A diene $C_{11}H_{16}$ was thought to have the structure below. Its UV spectrum showed a λ_{max} of 263 nm. Can the structure below be correct? If not, draw a structure with the same skeleton that satisfies the spectral data.



I

Heteroannuler dienes

II

Homoannular dienes

Answer: I not correct one because

215 + 4×5 + 5 = 240 nm, too far off. Probably due to wrong base system:

II is the correct one because :263 − 253 = 10 nm > 2×5, 2 alkyl substituents: