SPECTROCHEMICAL ANALYSIS

Calculation of λ_{max} : Woodward-Fieser rules

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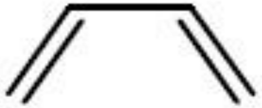
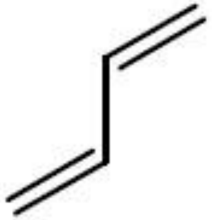
2022-2023

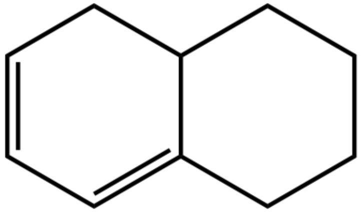
- Woodward-Fieser rules
  - Conjugated dienes and polyenes
  - α-β Unsaturated carbonyl compounds
  - Aromatic or benzoyl compounds

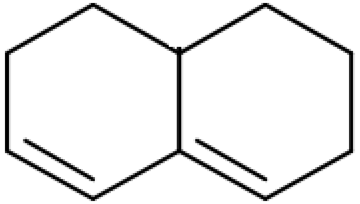
- Conjugated dienes
  - Acyclic dienes
    - Cisoid
    - Transoid
  - Cyclic dienes
    - Homo-annular
    - Hetero-annular

Basic values of λ_{max}


253 nm

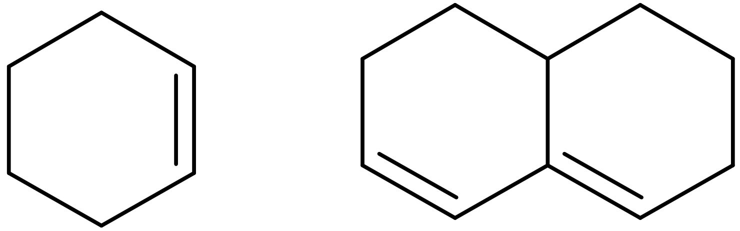

217nm


253 nm


214 nm

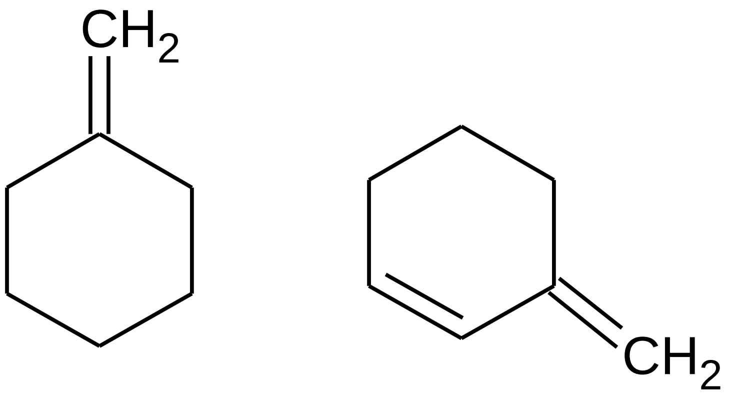
Endocyclic double bond

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



Exocyclic double bond

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



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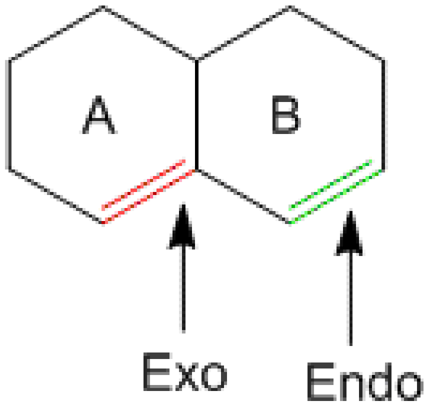

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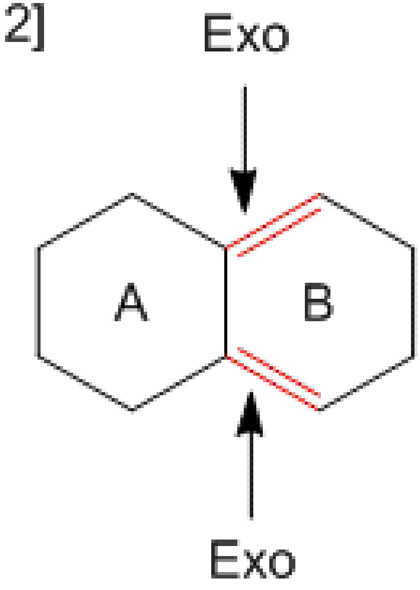

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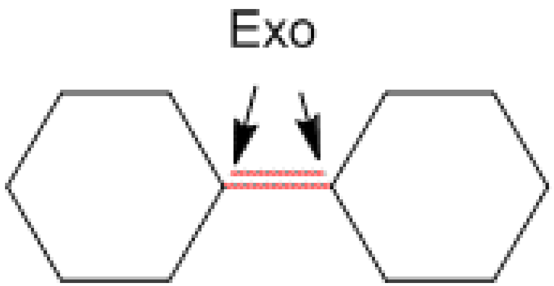
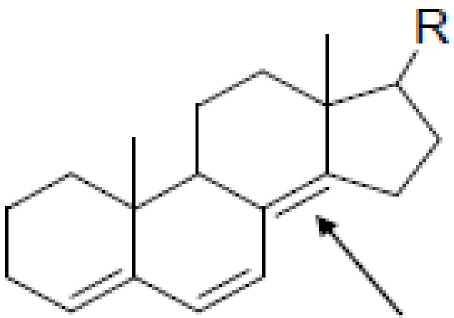
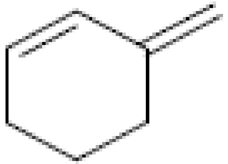


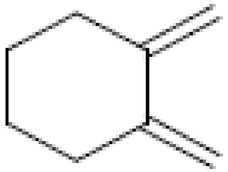
Increments:	**values**
For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
For each alkyl group	+ 5 nm
Auxochrome	
- OR	+ 6 nm
- O(C=O)R	0
- Cl	+ 5 nm
- Br	+ 5 nm
- SR	+ 30 nm
- NR_2	+ 60 nm
Phenyl ring	+ 60 nm



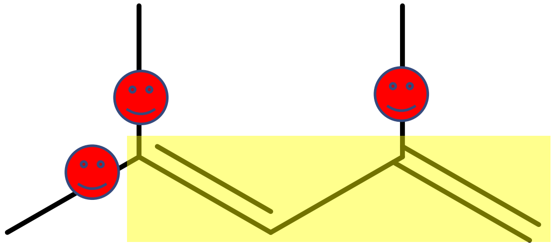
This compound has three exocyclic double bonds; the indicated bond is exocyclic to ***two*** rings



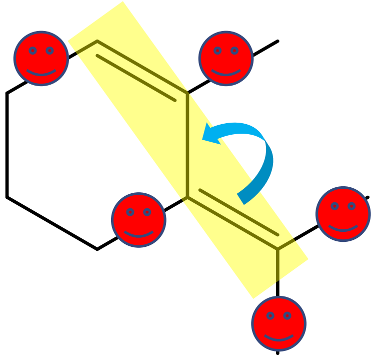
This is ***not*** a heteroannular diene; you would use the base value for an acyclic diene



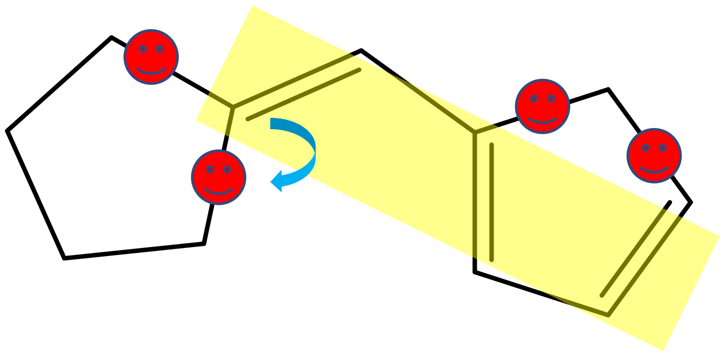
Likewise, this is ***not*** a homooannular diene; you would use the base value for an acyclic diene



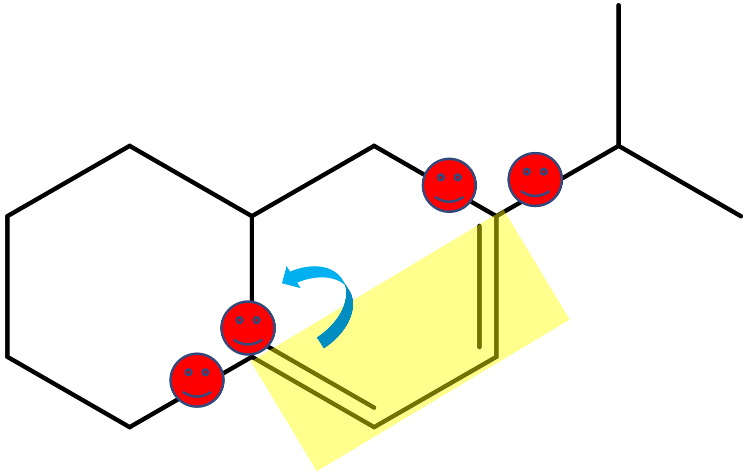
Acyclic diene	217
Alkyl subst.	3 x 5
Calculated value	232
Observed	234



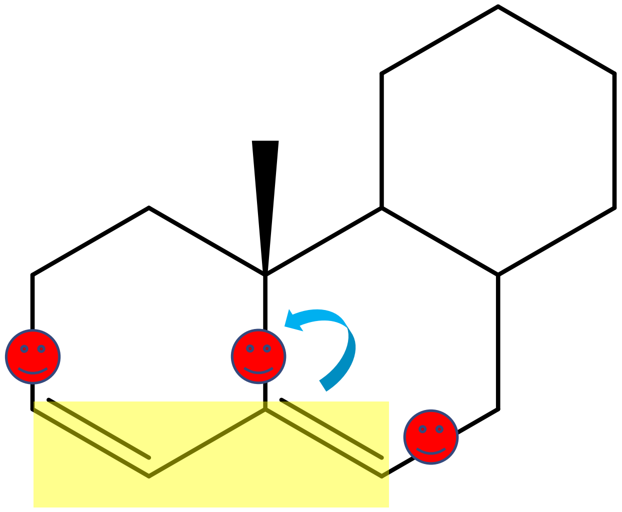
Acyclic diene	217 nm
Alkyl substitution	(5 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	247 nm



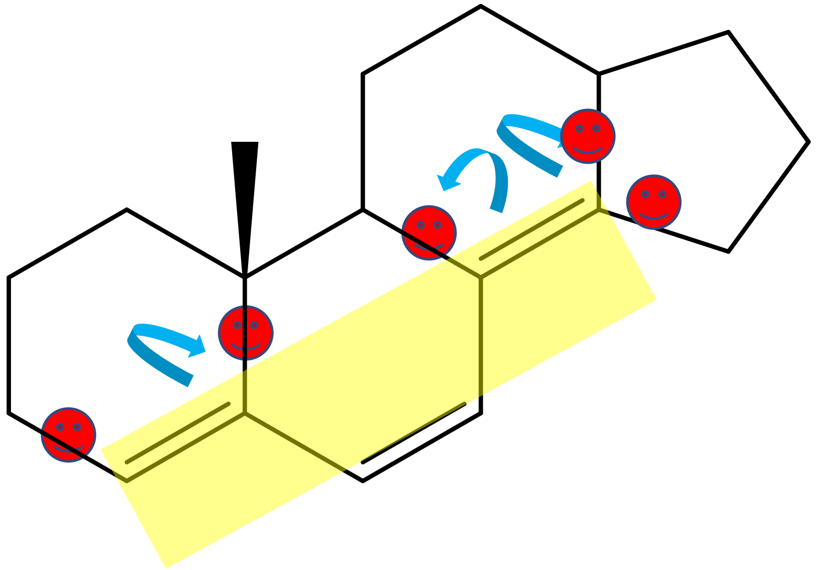
Homo-annular	**253 nm**
Alkyl substitution	(4 x 5) nm
Exocyclic double bond	(1 x 5) nm
Extra-conjugation	(1 x 30) nm
Calculated value	**308** nm



Homo-annular	**253 nm**
Alkyl substitution	(4 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	**278** nm
Observed value	275 nm



Hetero-annular	214 nm
Alkyl substitution	(3 x 5) nm
Exocyclic double bond	(1 x 5) nm
Calculated value	**234** nm
Observed value	235 nm

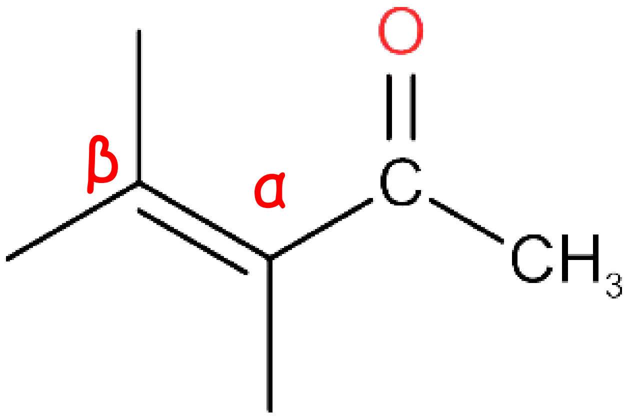


Hetero-annular	214 nm
Alkyl substitution	(5 x 5) nm
Exocyclic double bond	(3 x 5) nm
Extra conjugation	(1 x 30) nm
Calculated value	**284** nm

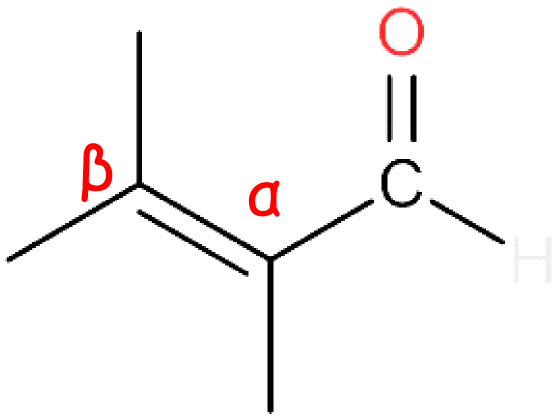
Woodward-Fieser rules

- Conjugated dienes and polyenes
- α-β Unsaturated carbonyl compounds
- Aromatic or benzoyl compounds

α-β unsaturated carbonyl compounds



Enone

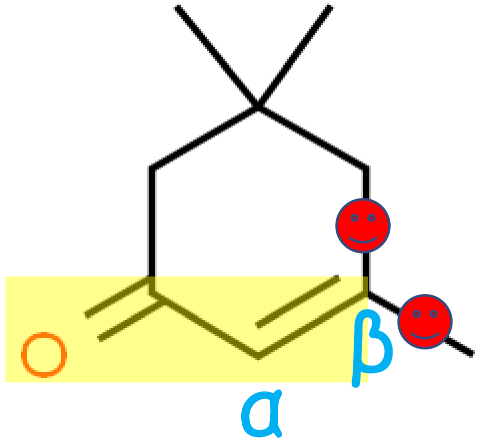


Enal

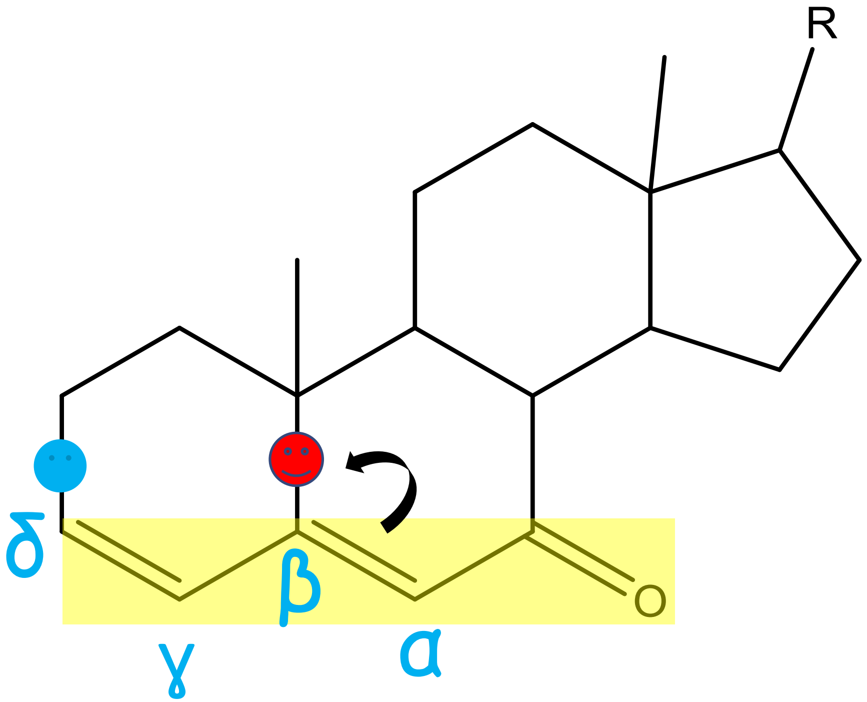
α-β unsaturated carbonyl compounds

Compounds	base values
α-β unsaturated aldehydes	210 nm
α-β unsaturated (carboxylic acids & esters)	195 nm
A cyclic α-β unsaturated ketones	215 nm
Cyclic α-β unsaturated ketones (six membered)	215 nm
Cyclic α-β unsaturated ketones (five membered)	202 nm
Increments:	**values**
For each additional conjugated double bond	+ 30 nm
For each exocyclic double bond	+ 5 nm
Homo-annular diene	+ 39 nm

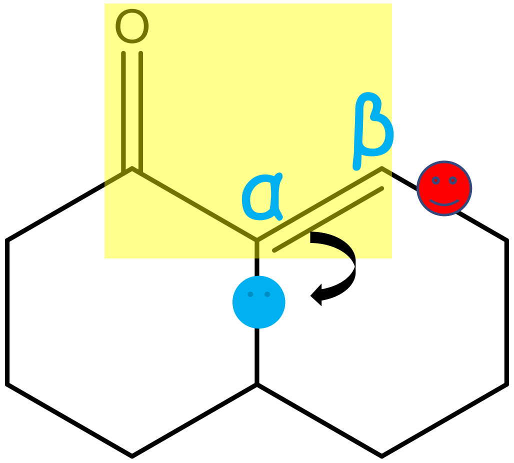
Substituent	α- position	β- position	γ- position	δ- position
Alkyl substituent or ring residue	10 nm	12 nm	18 nm	18 nm
- OH	35 nm	30 nm	50 nm	50 nm
-OAc	6 nm	6 nm	6 nm	6 nm
-OMe	35 nm	30 nm	17 nm	31 nm
-Cl	15 nm	12 nm	12 nm	12 nm
-Br	25 nm	30 nm	25 nm	25 nm
-SR	-	85 nm	-	-
$-NR_2$	-	95 nm	-	-



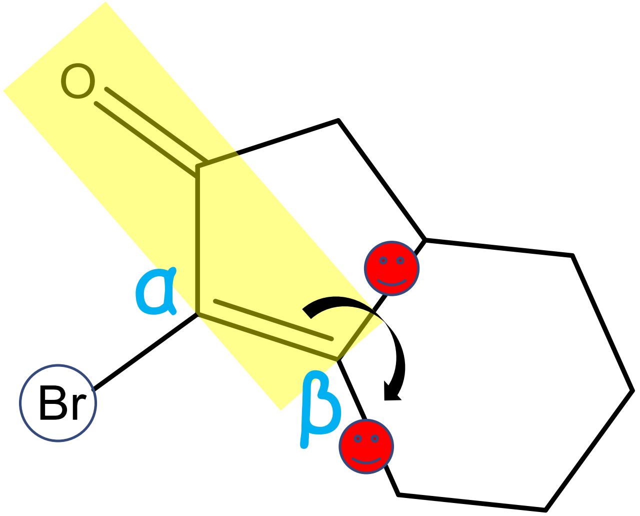
Six cyclic enone	**215 nm**
2 x β Alkyl substitution	(2 x 12) nm
Calculated value	239 nm
Experimental value	238 nm



Six cyclic enone	**215 nm**
Extra-conjugation	(1 x 30) nm
1 x β Alkyl substitution	(1 x 12) nm
1 x δ Alkyl substitution	(1 x 18) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**280 nm**



Six cyclic enone	**215 nm**
1 x α Alkyl substitution	(1 x 10) nm
1 x β Alkyl substitution	(1 x 12) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**242 nm**
Experimental value	238 nm

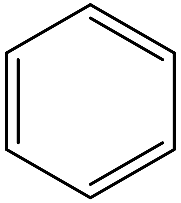


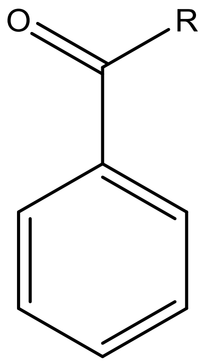
Five cyclic enone	**202 nm**
1 x α (Br) substitution	(1 x 25) nm
2 x β Alkyl substitution	(2 x 12) nm
Exo-cyclic double bond	(1 x 5) nm
Calculated value	**256 nm**

Woodward-Fieser rules

- Conjugated dienes and polyenes
- α-β Unsaturated carbonyl compounds
- Aromatic or benzoyl compounds

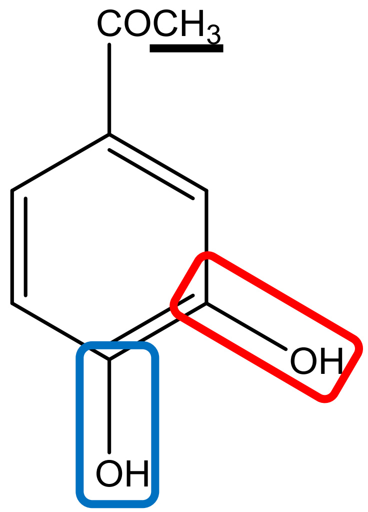
Aromatic or benzoyl compounds



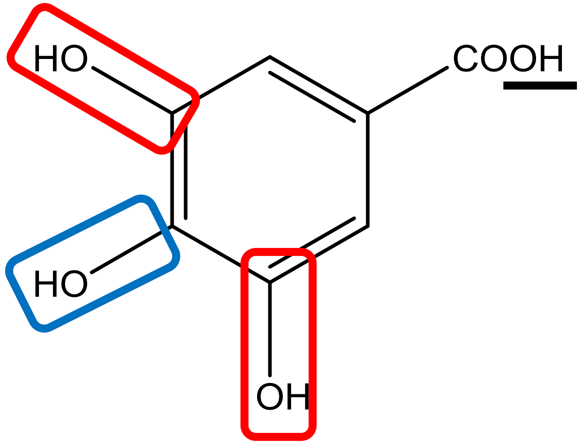


Parent chromophore	Basic value
R = alkyl or ring residue	246 nm
R = H	250 nm
R = OH or O-Alkyl	230 nm

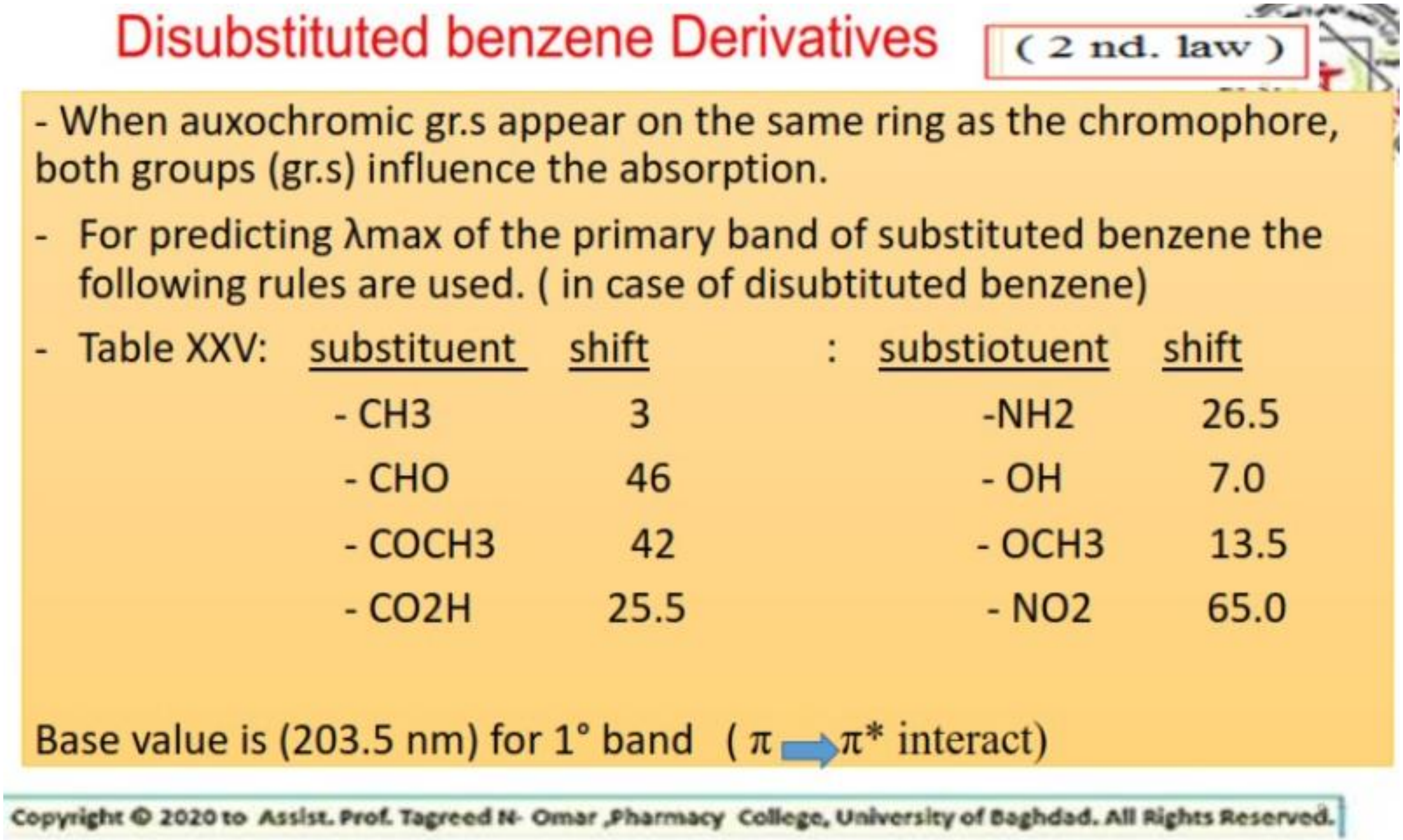
Substituent	o- position	m- position	p- position
Alkyl or ring residue	3 nm	3 nm	10 nm
- OH, -OR, O-ring	7 nm	7 nm	25 nm
-Cl	0 nm	0 nm	10 nm
-Br	2 nm	2 nm	15 nm
$-NH_2$	13 nm	13 nm	58 nm
$-NH(CO)CH_3$	20 nm	20 nm	45 nm
$-NHCH_3$	-	-	73 nm
$-NR_2$	20 nm	20 nm	85 nm



Base value of aromatic ketone	246 nm
Hydroxy group at m-position	7 nm
Hydroxy group at p-position	25 nm
Experimental value	278 nm



Base value of Ar-COOH	230 nm
Hydroxy group at m-position	(2 x 7) nm
Hydroxy group at p-position	25 nm
Experimental value	269 nm



Disubstituted benzene Derivatives

(2 nd. law)

- When auxochromic gr.s appear on the same ring as the chromophore, both groups (gr.s) influence the absorption.

- For predicting λmax of the primary band of substituted benzene the following rules are used. (in case of disubtituted benzene)

- Table XXV:

substituent	shift	substiotuent	shift
- CH_3	3	-NH_2	26.5
- CHO	46	- OH	7.0
- $COCH_3$	42	- OCH_3	13.5
- CO_2H	25.5	- NO_2	65.0

Base value is (203.5 nm) for 1° band ($\pi \rightarrow \pi^*$ interact)

A- For Para substitution

1- Both groups are e. donating EDG or e with drawing EWG: only the effect of the group causing the larger shift is used (so it is similar to monosubstituted benzene)

i.e P- nitrobenzenic acid

its λmax

Would be expected to be the same as that of nitro-benzene

Why ? because λmax parent cpd. = 203.5 nm

- CO2H 25.5 - NO2 65.0

$$\begin{array}{r} 203.5 \\ +\ 65 \\ \hline 268.5 \end{array}$$

268.5 nm ← 65 25.5

$NO2 > CO2H$

65 25.5

So if both the groups are electron-donating then the observed spectrum is closer to monosubstituted benzene. The group with stronger effect determines the extent of shifting of primary band.

B/Meta and ortho: if the two gr.s are *o*- or *m*- to one another the effect is usually the sum of the two individual effects (the shift effect are additive (meta : no resonance ….ortho steric effect)

So: by Uv: we can diff . between p & (-o,-m) derivetave…… no resonance

Note: -o,-m can not diff . between them by Uv

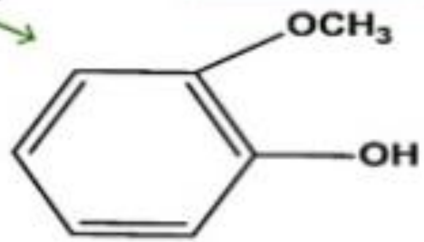
λmax.parent

p

OCH3= 13,5 > OH = 7 ⟶ x false

λmax=203,5+13.5=217nm √

o* the same as *m



λmax =203,5+13.5 +7 =224nm

Applications of Ultraviolet and Visible Spectroscopy

- ☐ A few functional groups (chromophores) may be detected by the UV-visible spectroscopy, but it is especially useful for detecting the presence and elucidating the nature of conjugated systems including aromatic rings.
- ☐ In the application of the electronic spectroscopy for structural analysis, only the region above 200 nm is really useful and the region below 200 nm is hardly useful for this purpose.

Some important applications of UV and visible spectroscopy to organic chemistry are summarized as follows.

1. Detection of a Functional Group (Chromophore)

- The presence or absence of a particular chromophore may be indicated by the presence or absence of an absorption band in the expected wavelength region.
- For example, the presence of a low intensity band in the region 270-300 nm indicates the presence of an aldehydic or ketonic carbonyl group. If the spectrum is transparent above 200 nm, it shows the absence of

  (a) an aldehydic or ketonic carbonyl group.

(b) a conjugated-system.

(c) an aromatic ring.

(d) 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 characterized by their absorptions above 200 nm.
- The longer the conjugated system, the higher the λ_{max} and ε_{max} values
- Substitutions on a conjugated system generally cause bathochromic and hyperchromic effects.
- Thus, we can elucidate the nature of conjugation by comparing the values of λ_{max} and ε_{max} for the compound under study with that of a probable analogous compound.

3. Study of Extent of Conjugation

- The values of λ_{max} and ε_{max} increase as the number of conjugated multiple bonds increases, thus the 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.

4. Distinction Between Conjugated and Unconjugated Compounds

5. Study of Strain

- In molecules like 2-substituted biphenyls, there is steric strain which forces the rings out of coplanarity 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 Configurations of Geometrical Isomers

- It is possible when there is loss of coplanarity of one isomer due to steric hindrance resulting in the loss of conjugation accompanied by hypsochromic and hypochromic effects.
- Obviously, this isomer is the cis-isomer in which groups are closer to each other to cause steric strain and to force the groups out of coplanarity. Thus, cis-isomers absorb at shorter wavelengths and have lower intensity than the trans-isomers

7. Study of Tautomerism

- UV spectroscopy can be used for identifying the predominant (stable) tautomer.

8. Confirmation of Suspected Phenols and Aromatic Amines

- The spectral characteristic of phenols and aromatic amines change with the change of pH of the solution.
- Thus, suspected phenols and aniline derivatives may be confirmed by comparison of UV spectra recorded in neutral and alkaline or acid solutions.

9. Study of Structural Features in Different Solvents