

B.Sc Part II Paper ORGANIC

TOPIC: - SPECTRO SCOPY

COLLEGE: - PATNA SCIENCE COLLEGE, PATNA
DEPARTMENT OF CHEMISTRY

BY: - DR. PANKAJ KUMAR (GUEST FACULTY)

EMAIL ID: - pank9097@gmail.com

MOB NO: - 9097705750

SPECTROSCOPY

Woodward Rule For calculating λ_{\max} in Conjugated dienes, trienes and Polyenes.

Woodward gave certain empirical rule for calculating the λ_{\max} in conjugated dienes, trienes and polyenes.

According to these rule, Each dienes has a certain fixed basic value and its actual λ_{\max} depends upon the following factors.

- i.) The no. of Alkyl substituents or ring residues present on the diene system.
 - ii.) The number of double bonds extending conjugation beyond the diene system.
 - iii.) The presence Auxochromes i.e. The Polar groups such as -Cl, Br, -OR, -NH₂, -OCOCH₃ etc.
- The contribution By the different substituents or Auxochromes it present is added to the λ_{\max} value net value of λ_{\max} .

Value of λ_{\max} for different substituent.

Parent open chain diene ————— 217 nm.

Parent Heteroannular diene _____ 214nm.

Parent Homoannular diene _____ 253 nm.

For Each Double Bond Extending Conjugation add _____ 30 nm.

For Each Alkyl substituent (R) or Ring Residue add _____ 5 nm.

For Each Exocyclic Double Bond Add _____ 5 nm.

Auxochromes

For an OAC add _____ 0 nm.

For an OR add _____ 6 nm.

For an SR add _____ 30 nm.

For CL or BR atom add _____ 5 nm.

Ques :- Calculate the λ_{\max} in the UV Spectrum of 2,4- Hexadiene.

Solution :- $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$

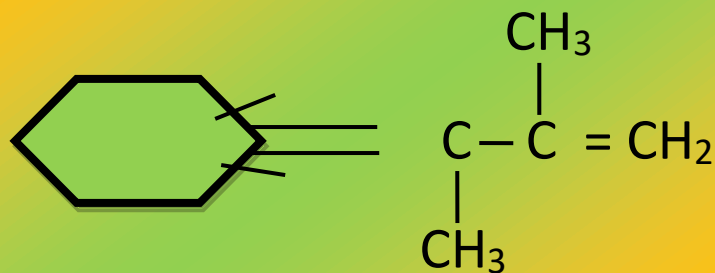
The Parent unit of 2,4 – Hexadiene is a Butadiene. It has Two Methyl Substituent attached to either side. Its λ_{max} can be calculated using Woodward's Rule as under,

Basic value = 217 nm.

2 Alkyl substituents (2×5) = 10 nm.

Total calculated λ_{max} = 227 nm.

Ques:- What λ_{max} value do you expect for the following compound ?



Solution :- It is a conjugated diene system which has two alkyl substituents , two ring residues , one exocyclic double bond.

Basic Value = 217 nm.

2 Alkyl substituents (2×5) = 10 nm.

2 Ring Residue = 10 nm.

One exocyclic double bond = 5 nm.

Total calculated $\lambda_{\max} = (217+10+10+5) \text{ nm.} = 242 \text{ nm.}$

Ques :- Calculate λ_{\max} for



Solution :- It is an example of hetroannular diene and there are four ring residues on the double bond.

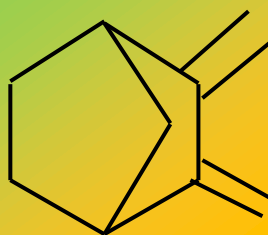
Thus,

Basic value = 215 nm.

Four ring Residue (4×5) = 20 nm.

Calculated value = 235 nm.

Question :- Calculate the absorption maximum in the ultraviolet spectrum of 2,3 – dimethylene bicyclo [2,2,1] heptanes.



Solution :- The of absorption maximum for this compound is calculated as :

Basic value	= 217 nm
2 - Rind residues	(2×5) = 10 nm
2 – Exoxylic double bond	= 10 nm
1 – Bicyclic system	= 15 nm
Calculated Value	<hr/> = 252 nm <hr/>

• CHROMOPHORE AND AUXOCHROME

Chromophore - Chromophore was considered as a functional group which is capability or property to impart a colour to a compound. In a broader sense, a chromophore is defined as a group which absorbs electromagnetic radiation in the visible or uvrange some prominent chromophore along with their λ_{\max} α_{\max} listed in the following table :

<u>Chromophore</u>	<u>Transition</u>	<u>λ_{\max} (nm)</u>	<u>α_{\max}</u>	<u>Solvent</u>
>C=C<	$\pi - \pi^*$	175	15000	Vapour
$-\text{C}\equiv\text{C}-$	$\pi - \pi^*$	175	10000	Hexane
$-\text{C}=\text{O}$	$\pi - \pi^*$	180	10000	Hexane
	$n - \sigma^*$	160	18000	
$\begin{array}{c} \text{OH} \\ \\ -\text{C}=\text{O} \end{array}$	$n - \pi^*$	285	15	
$-\text{N}=\text{N}-$	$n - \pi^*$	205	60	Methanol
$-\text{NO}_2$	$n - \pi^*$	338	5	Ethanol
	$n - \pi^*$	274	15	Methanol

Auxochrome :- An auxochrome is a group which when attaché to chromophore shift to absorption maximum toward longer wavelengths alongs with an increase in the intensity of absorption.

By it self, it does not show any absorption above 200 nm .

Thank you