ULTRAVIOLET SPECTROSCOPY

SEM-4, CC-8
PART-3, PPT-4

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Rules for Calculation of λ_{max} for the following systems

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(Dienes, Aldehydes and Ketones)

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ULTRAVIOLET SPECTROSCOPY (PART-3, PPT-4)

Application of Woodward's Rules for Calculation of λ_{max}

In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as **Woodward-Fieser Rules**. It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore. By this rule the expected value of absorption maxima (λ_{max}) of cyclic as well as acyclic dienes are calculated.

Longer the conjugated system, greater is the wavelength of absorption maximum (λ_{max}). The intensity of absorption (ε_{max}) also increases with the increase of the *chromophore*. Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the *Base value or Parent value*. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as -Cl, -Br, etc., are added to the basic value to obtain λ_{max} for a particular compound. The presence of alkyl group on the double bond (alkyl substituent or Ring Residue) also causes Bathochromic shift. Ring residue is a C-C bond, not a part of the conjugated system but attached to any one of the carbon atoms of the conjugated polyene system.

Various Types of Double Bonds in Conjugation

1. Alicyclic diene or dienes contained in an open chain system, i.e., where basic unit is butadiene system.

2. Homoannular conjugated double bonds are the cyclic diene having conjugated double bonds present in the same ring. It is also called Homodiene.

3. Heteroannular conjugated double bonds are the cyclic diene having conjugated double bonds which are present in the different rings.

4. Exocyclic and Endocyclic conjugated double bonds: Exocyclic double bond is a double bond, part of the conjugated system, formed by any carbon atom of any ring but present outside the ring. Endocyclic double bond is present inside the ring. The various types of double bonds are shown in Figure 1.


Figure 1: Types of conjugated double bonds

	Here Ring A has one exocyclic and one endocyclic double bond. Ring B has one endocyclic double bond, but no exocyclic double bond.
	Here Ring A has two endocyclic double bonds, but no exocyclic double bond. Ring B has one exocyclic double bond, but no endocyclic double bond.
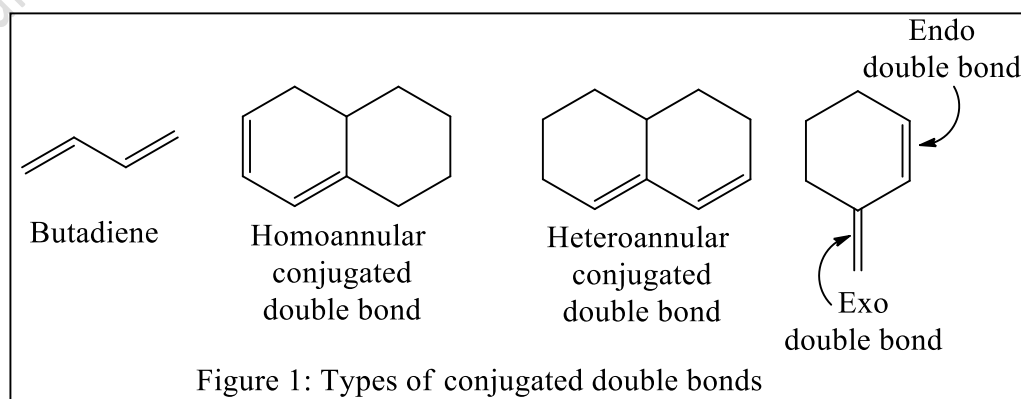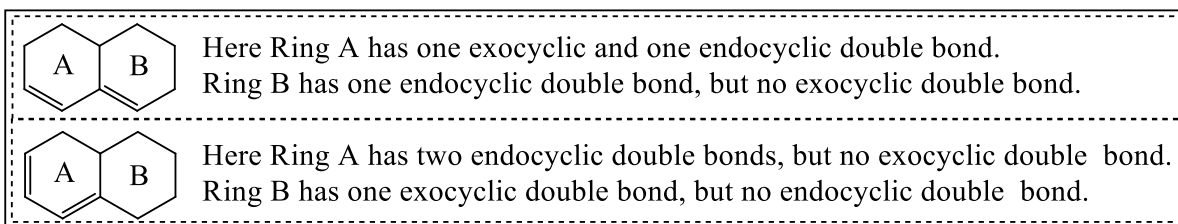
Symmetry Properties of Molecular Orbitals in a Conjugated Diene

The wavefunctions (π MOs) of buta-1,3-diene can be represented in *s-trans* or *s-cis* conformation. The butadiene π MOs are more stable in *s-trans* conformation. The *HOMO*/*LUMO* energies in *s-trans* and *s-cis* conformations of buta-1,3-diene are not the same. In *s-cis* conformation, the *HOMO* energy is raised and the *LUMO* energy is lowered relative to those in the *s-trans* form (Figure 2).

Unlike the *s-trans* form, the *s-cis* conformation has a possible interaction between the two terminal p-orbitals. An antibonding interaction raises the *HOMO* energy, while a bonding interaction lowers the *LUMO* energy in *s-cis* conformation.

Figure 2: Relative energies of frontier orbitals in *s-trans* and *s-cis* conformations of buta-1,3-diene
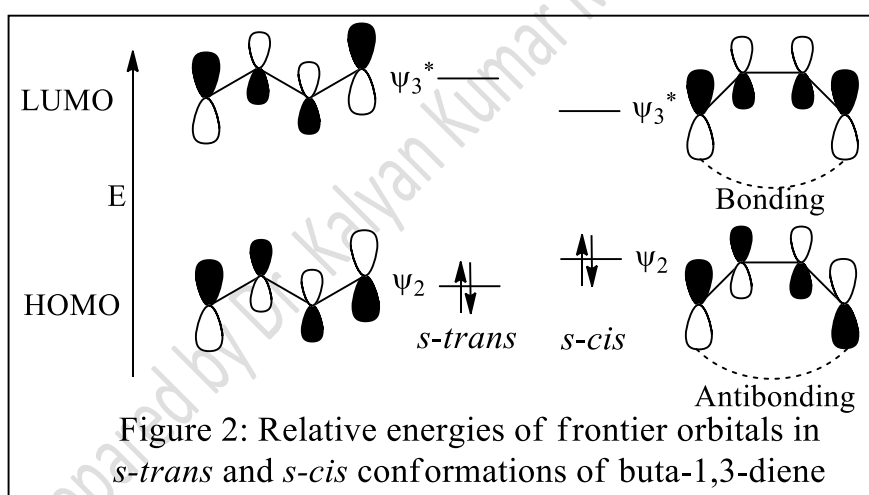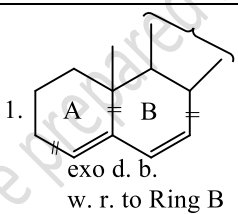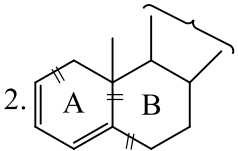
The lower *HOMO/LUMO* energy gap in *s-cis* conformation leads to UV absorption at a longer wavelength (253 nm) for a *homoannular diene* locked in *s-cis* conformation compared with a λ_{max} of 214 nm for an acyclic or a *heteroannular diene* existing predominantly or exclusively in *s-trans* conformation.

Group Contribution

<table>
<tr><td colspan="4" align="center">Base Value</td></tr>
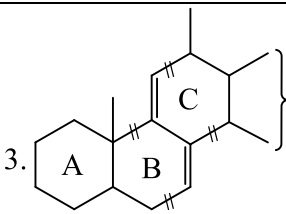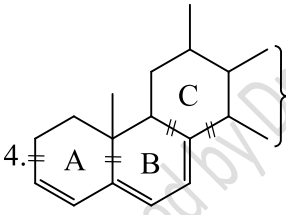<tr><td>(i)</td><td colspan="2">Value assigned for parent heteroannular or open chain diene</td><td>214 nm (or 217 nm)</td></tr>
<tr><td>(ii)</td><td colspan="2">Value assigned for parent homoannular diene</td><td>253 nm</td></tr>
<tr><td>(iii)</td><td colspan="3" align="center">Increment for</td></tr>
<tr><td></td><td>(a)</td><td>Each alkyl substituents or Ring Residue</td><td>5 nm</td></tr>
<tr><td></td><td>(b)</td><td>The exocyclic nature of any double bond</td><td>5 nm</td></tr>
<tr><td></td><td>(c)</td><td>A double bond extending conjugation</td><td>30 nm</td></tr>
<tr><td></td><td colspan="2" align="center">Increment of Auxochromes</td><td></td></tr>
<tr><td></td><td>(i)</td><td>- OAc</td><td>0 nm</td></tr>
<tr><td></td><td>(ii)</td><td>- OR</td><td>6 nm</td></tr>
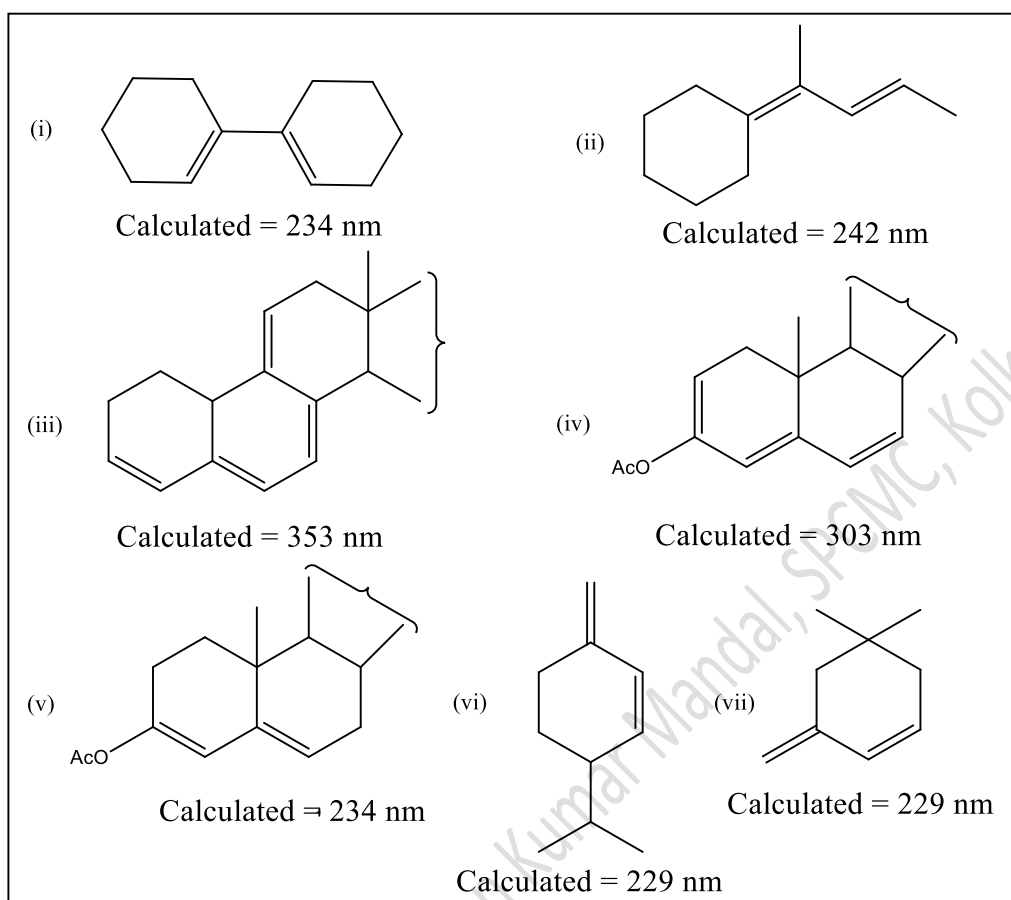<tr><td></td><td>(iii)</td><td>- SR</td><td>30 nm</td></tr>
<tr><td></td><td>(iv)</td><td>- NR_2</td><td>60 nm</td></tr>
<tr><td></td><td>(v)</td><td>- Cl, - Br</td><td>5 nm</td></tr>
</table>

Calculation of λ$_{max}$ for Conjugated Diene

	nm
1. (structure: rings A = B =, exo d. b. w. r. to Ring B)	
Parent diene (Heteroannular)	214
Ring residue x 3 (5 nm x 3)	15
Exocyclic double bond x 1	5
Total	234
Observed	235

	nm
2.	
Parent diene (Homoannular)	253
Ring residue x 3 (5 nm x 3)	15
Exocyclic double bond x 1	5
Total	273
Observed	275

|	nm
3.	
Parent diene (Heteroannular)	214
Ring residue x 4 (5 nm x 4)	20
Exocyclic double bond x 2	10
Total	244
Observed	245

	nm
4. Observed λ_{max} = 315 nm	
Parent diene (Homoannular, Ring B)	253
Ring residue x 4 (5 nm x 4)	20
Exocyclic double bond x 2	10
Double bond extending conjugation	30
Total	313

Calculate λ_max for the following Compounds

(i) Calculated = 234 nm

(ii) Calculated = 242 nm

(iii) Calculated = 353 nm

(iv) Calculated = 303 nm

(v) Calculated = 234 nm

(vi) Calculated = 229 nm

(vii) Calculated = 229 nm

Woodward's Enone and Dienone Rules for Calculation of λ_max

Woodward and Fieser framed certain empirical rules for calculating the absorption maximum for an α,β-unsaturated carbonyl compounds. The rules were later modified by Scott.

Enone   Dienone
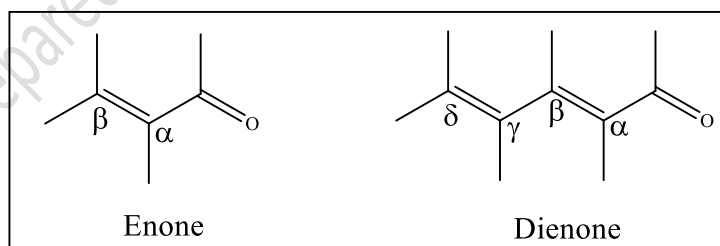
Conjugation of the carbonyl group with double bonds shift both $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions to longer wavelength. The effect on $\pi \rightarrow \pi^*$ is more pronounced.
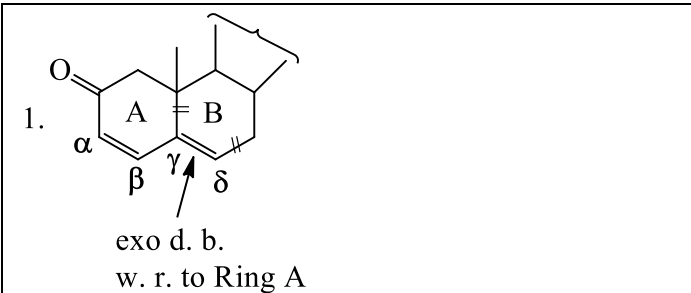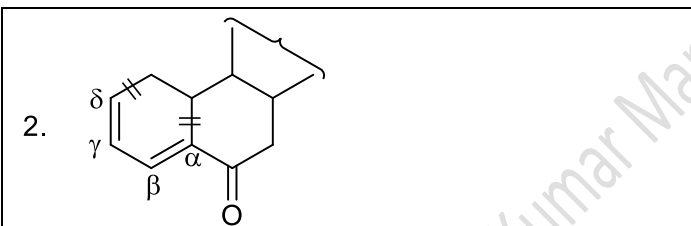
Group Contribution

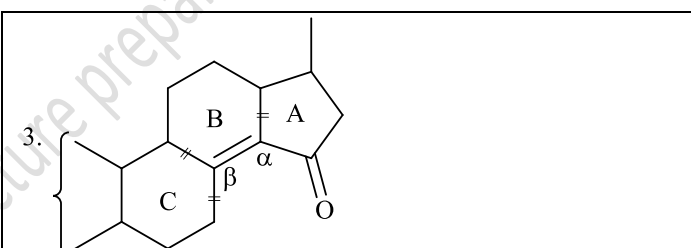| Base Value		
(i)	Value assigned for Acyclic α,β-unsaturated ketone	215 nm
(ii)	Value assigned for 6-membered cyclic α,β-unsaturated ketone	215 nm
(iii)	Value assigned for 5-membered cyclic α,β-unsaturated ketone	202 nm
(iv)	Value assigned for 5-membered cyclic α,β-unsaturated ketone with exocyclic double bond	215 nm
(v)	Value assigned for α,β-unsaturated aldehyde	210 nm

Increment for				
(i)	A double bond extending conjugation	30 nm		
(ii)	The exocyclic nature of any double bond	5 nm		
(iii)	The Homodiene component	39 nm		
(iv)	Alkyl group or Ring residue	α	β	γ or higher
		10	12	18
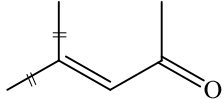
Group	α	β	γ	δ
-OH	35	30	30	50
-OR	35	30	17	31
-OAc	6	6	6	6
-SR	-	85	-	-
-NH₂, -NHR, -NR₂	-	95	-	-
-Cl	15	12	12	12
-Br	25	30	25	25

Calculation of λ_max for Conjugated Carbonyl Compounds

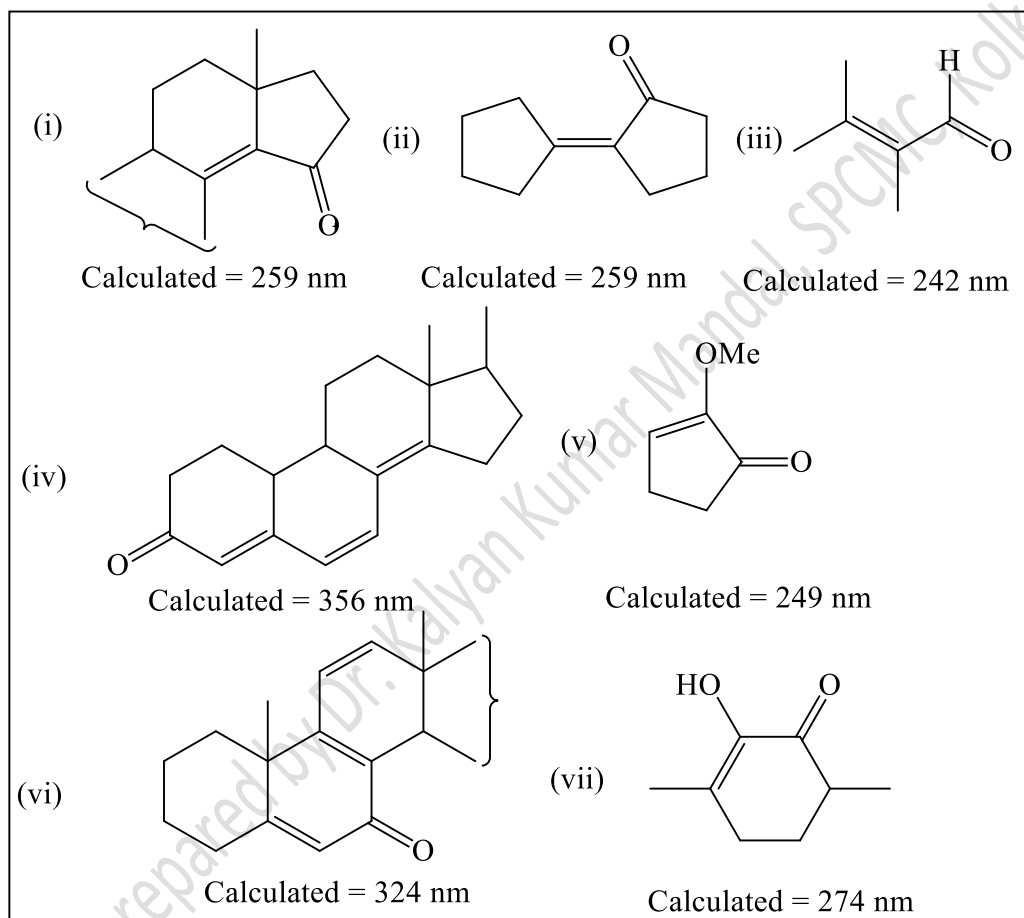|	**nm**
1.	
Basic value for 6-membered cyclic α,β-unsaturated ketone	215
Double bond extending conjugation	30
Ring residues, γ-substitution	18
δ-substitution	18
Exocyclic double bond	5
Total	286

	nm
2.	
Basic value for 6-membered cyclic α,β-unsaturated ketone	215
Double bond extending conjugation	30
Ring residues, α-substitution	10
δ-substitution	18
Exocyclic double bond	5
Presence of homodiene component	39
Total	317

	nm
3.	
Basic value for 5-membered cyclic α,β-unsaturated ketone with exocyclic double bond	215
Ring residues, α-substitution	10
β-substitution x 2 (12 x 2)	24
Exocyclic double bond x 2 (5 x 2 nm)	10
Total	259

		nm
4.		
Basic value for α,β-unsaturated ketone		215
Ring residues, β-substitution x 2 (12 x 2)		24
	Total	239

Calculate λ_{max} for the following Compounds

Calculate λ_{max} for the following Compounds

(i) Calculated = 259 nm

(ii) Calculated = 259 nm

(iii) Calculated = 242 nm

(iv) Calculated = 356 nm

(v) Calculated = 249 nm

(vi) Calculated = 324 nm

(vii) Calculated = 274 nm