(v) Heptane. Due to only σ—σ* transition, there is no absorption in the UV range.

(vi) Aniline. Due to the presence of auxochrome, NH_2 group, attached to benzene, it shows absorption at about 280 nm.

(vii) Butadiene. It contains a conjugated system and shows strong absorption at about 217 nm.

Example 1.2. *The UV spectrum of acetaldehyde has two peaks of* λ_{max} = 290 nm *and* λ_{max} = 180 nm. *What type of electronic transitions is responsible for each of these transitions ?*

Solution. λ_{max} = 290 nm is due to $n \rightarrow \pi^*$ transition

λ_{max} = 180 nm is due to $\pi \rightarrow \pi^*$ transition.

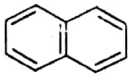
Problem 1.2. *Of the following compounds, which can absorb UV radiation :*

(i) Benzene (ii) 1,3-Pentadiene (iii) Heptane (iv) Ethanol (v) Ethylene (vi) Benzoic acid (vii) Nitrobenzene (viii) Water.

[**Ans.** (*i*) (*ii*), (*v*), (*vi*) and (*vii*)]

Problem 1.3. *Which of the following compounds would you expect to exhibit UV absorptions in the 200¬400 nm range :*

(i) 1,3-cyclohexadiene (ii) 1,4-cyclohexadiene (iii) Cyclohexene (iv) Naphthalene.

Ans. 1, 3-Cyclohexadiene  and naphthalene  would exhibit UV absorption in the 200-400 nm range because they contain conjugated double bonds and would therefore undergo $\pi \rightarrow \pi^*$ transition in the 200-400 nm range.

Problem 1.4 *Two isomeric ketones having the formula* $CH_2=CH-\underset{\displaystyle CH_3}{\underset{|}{CH}}COCH_3$ and $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}=C-COCH_3$ *were subjected to ultraviolet spectroscopy. One isomer exhibited* λ_{max} 235 nm (ε_{max} 12000) *while the other did not show any high intensity absorption above 200* nm. *Which isomer shows* λ_{max} 235 nm (ε_{max} 12000) ?

Ans. The isomer $CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-\overset{\displaystyle O}{\overset{||}{C}}-CH_3$ would show high intensity absorption above 200 nm due to $\pi-\pi^*$ transition in a conjugated systems. Therefore it shows λ_{max} 235 *nm* (ε_{max} 12000).

The other isomer contains isolated ethylenic bond and carbonyl group. Due to ethylenic bond it can have $\pi \rightarrow \pi^*$ transition only below 200 nm. Due to carbonyl group, it can have $\pi \rightarrow \pi^*$ transition above 200 nm but it would of very low intensity.

1.12. WOODWARD-FIESER RULES FOR CALCULATING ABSORPTION MAXIMA*

By studying the ultraviolet absorption spectra of a large number of compounds, Woodward (1941) deduced certain rules for correlating λ_{max} with molecular structure. Since then, these rules have been modified by Scott and Feiser as a result of more experimental data. The modified rules known as Woodward-Fieser rules, enable us to calculate the position of λ_{max} for a given structure by relating the position of λ_{max} with the position and degree of substitution of chromophore.

The calculated values are generally within 2 or 3 nm of experimental values.

We will now consider these rules briefly for different classes of compounds.

1.13. WOODWARD-FIESER RULES FOR CALCULATING λ_{max} IN CONJUGATED DIENES, TRIENES AND POLYENES

Before we consider the rules for dienes, trienes, etc., it will be useful to explain some terms involved in discussing the rules.

(1) **Homoannular diene.** *It is a cyclic diene which contains conjugated double bonds in the same ring.*

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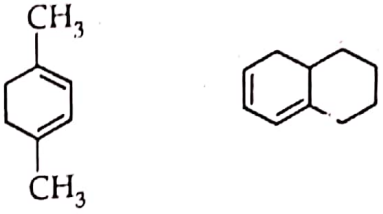
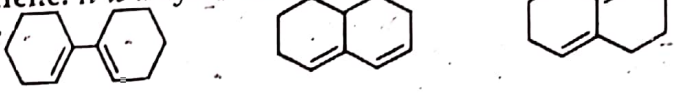
*Not included in the syllabus of various universities of Punjab

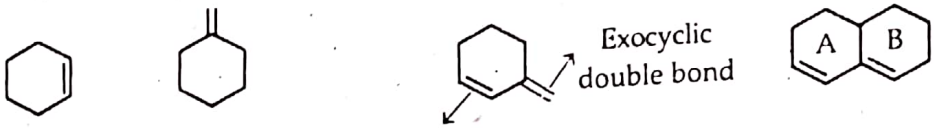
For example :



(2) **Heteroannular diene.** *It is a cyclic diene in which double bonds in conjugation are present in different rings. For example :*



(3) **Endocyclic double bond.** *It is a double bond present in a ring as shown below* in (*a*).



Endocyclic double bond (*a*) | Exocyclic double bond (*b*) | Endocyclic double bond (*c*) | Ring A has one endocyclic and one exocyclic double bond. Ring B has one endocyclic double bond only. (*d*)

(4) **Exocyclic double bond.** *It is a double bond in which* **one** *of the doubly bonded atoms is a part of a ring system as shown above in (b).*

WOODWARD-FIESER RULES FOR CONJUGATED DIENES, TRIENES, POLYENES, ETC.

According to these rules, *each type of diene or triene system has a certain fixed value at which absorption takes place.* This constitutes the **basic value** or **parent value.**

The contributions made by various alkyl substituents or ring residues, double bonds extending conjugation and polar groups such as —Cl, —Br and —OR are added to the basic value to get λ_{max} for a particular compound.

The parent values and contributions of different substituents/groups are given in table 1.3.

Table 1.3. Parent values and increments for different substituents/groups.

(*a*) **Parent Values**		
(*i*) *Acyclic conjugated diene*		217 nm
(*ii*) *Homoannular conjugated diene*		253 nm
(*iii*) *Heteroannular conjugated diene*		214 nm
(*b*) **Increments**		
(*i*) Each alkyl substituent or ring residue		5 nm
(*ii*) Exocyclic double bond		5 nm
(*iii*) Each double bond extending conjugation		30 nm
(*c*) **Auxochromes :**	—OR	6 nm
	—SR	30 nm
	—Cl, —Br	5 nm
	$—NR_2$	60 nm
	$—OCOCH_3$	0 nm

To illustrate the above rules, a few examples are given ahead :

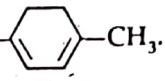
Example 1.3. *On the basis of Woodward–Fieser rules, calculate λ_{max} for 2, 4-hexadiene,* $CH_3-CH=CH-CH=CH-CH_3$.

Solution. 2, 4-Hexadiene is an acyclic conjugated diene having two methyl substituents attached to either side of the conjugated system as shown bellow :

$CH_3-CH=CH-CH=CH-CH_3$

∴ Parent value for acylic conjugated diene		= 217 nm
Two alkyl substituents,	2×5	= 10 nm
Calculated value of λ_{max}		= 227 nm

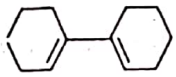
Observed value of λ_{max} for 2, 4-hexadiene is **227 nm.**

Example 1.4. *Calculate λ_{max} for 1, 4-dimethylcyclohexa-1, 3-diene,*  .

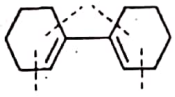
Solution. The given compound is a homoannular diene having two alkyl substituents and two ring residues (as shown below by dotted lines).

∴ Parent value for homoannular diene		= 253 nm
Two alkyl substituents,	2×5	= 10 nm
Two ring residues,	2×5	= 10 nm
∴ **Calculated value**		= **273 nm**
Observed value		= **265 nm**

Example 1.5. *Compute λ_{max} for the compound :*

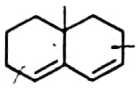


Solution. The given compound is a heteroannular diene having 4 ring residues as shown below.

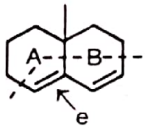


∴ Parent value for heteroannular diene		= 214 nm
Four ring residues	4×5	= 20 nm
∴ **Calculated value**		= **234 nm**
Observed value		= **236 nm**

Example 1.6. *Calculate λ_{max} for the compound having the structure :*

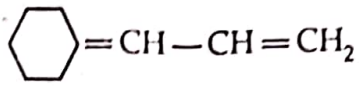


Solution. According to the given structure, it represents a heteroannular diene having three ring residues and one exocyclic double bond marked *e* (This double bond is exocyclic with respect to ring B). That is :

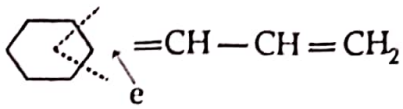


∴ Parent value for heteroannular diene		= 214 nm
Three ring residues,	3 × 5	= 15 nm
One exocyclic double bond		= 5 nm
∴ **Calculated value**		= 234 nm
Observed value		= 235 nm

Example 1.7. Calculate λ_{max} for 3 – cyclohexylidenepropene

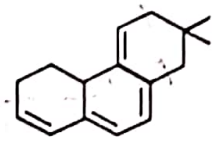


Solution. 3 -Cyclohexylidenepropene is a conjugated diene having two ring residues and an exocyclic double bond marked shown below.

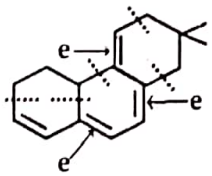


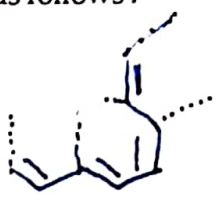
∴ Parent value for conjugate diene		= 217 nm
Two ring residues	2 x 5	= 10 nm
One exocyclic double bond		= 05 nm
∴ **Calculated value**		= 232 nm
Observed value		= 236.5 nm

Example 1.8. Compute λ_{max} for the following compound :



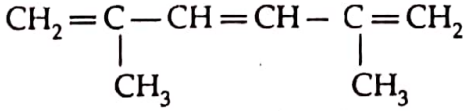
Solution . The λ_{max} for given compound may be computed as follows :





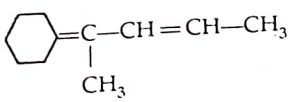
1 ∴ Parent value of homoannular diene		= 253 nm
3 Five ring residues		5 × 5 = 25 nm
4 Three exocylic double bonds (maked *e*)		3 × 5 = 15 nm
2 Two double bonds extending conjugation		2 × 30 = 60 nm
Calculated value		= 353 nm

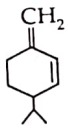
Problem 1.5. *Calculate λ_{max} for 2, 5-dimethylhexa –1, 3, 5-triene.*

Ans. The given compound is 

Parent acyclic conjugated diene (217) + 2 alkyl substituents (2 × 5) + double bond extending conjugation (30) = 217 + 10 + 30 = 257 nm.

Problems 1.6. *Calculate λ_{max} for the following compounds :*

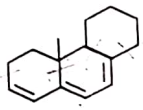
(*i*) 

(*ii*) 

[**Ans.** (*i*) Parent conjugated diene + 2 alkyl substituents + 2 ring residues + exocyclic double bond = 217 + 10 + 10 + 5 = 242 nm

(*ii*) Parent heteroannular diene + 2 ring residues + exocyclic double bond = 214 + 10 + 5 = 229 nm]

Problem 1.7. *Compute λ_{max} for the following compound.*



[**Ans.** Parent homoannular diene + Four ring residues + Two exocyclic double bonds + one double bond extending conjugation = 313 nm.]

1.14. WOODWARD-FIESER RULES FOR α, β-UNSATURATED CARBONYL COMPOUNDS

Woodward-Fieser rules for calculating λ_{max} for α, β-unsaturated carbonyl compounds modified by Scott may be summed up as given in table 1.4.

Table 1.4. Parent values and increments for different substituents/groups

(a)	**Parent Values**			
	(*i*) *α, β-unsaturated acyclic or six membered ring ketone*			215 nm
	(*ii*) *α, β-unsaturated five-membered ring ketone*			202 nm
	(*iii*) *α, β-unsaturated aldehyde*			207 nm
(b)	**Increments**			
	(*i*) Each alkyl substituent or ring residue			
	at α position			10 nm
	at β position			12 nm
	at γ and higher positions			18 nm
	(*ii*) Each exocyclic double bond			5 nm
	(*iii*) Double bond exocyclic to two rings simultaneously			10 nm
	(*iv*) Double bond extending conjugation			30 nm
	(*v*) Homoannular conjugated diene			39 nm
	(*vi*) **Auxochromes :**	Position		
		α	β	γ
	—OH	35	30	50
	—OR	35	30	17
	—SR	—	85	—
	—$OCOCH_3$	6	6	6
	—Cl	15	12	—
	—Br	25	30	—
	—NR_2	—	95	—

In these compounds, the actual spectra obtained are affected considerably by the nature of the solvent employed. Therefore, a solvent correction is applied to the calculated value to obtain the value for that particular solvent. However, we are not discussing the solvent corrections at this stage.

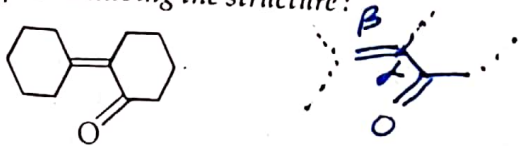
A few examples are given below for the sake of illustration of the above rules :

Example 1.9. *Calculate* λ_{max} *for the compound* $CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{\alpha}{|}}{C}=\overset{\overset{\beta}{|}}{CH_2}$ $\quad CH_3$

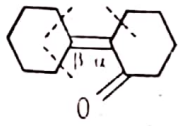
Solution. The given compound is an α, β-unsaturated acyclic ketone having an alkyl substituent in α-position.

∴ Parent value for α, β-unsaturated acyclic ketone		= 215 nm
One alkyl substituent in α-position		= 10 nm
∴ **Calculated value**		= **225 nm**
Observed value		= **220 nm**

Example 1.10. *Compute* λ_{max} *for the compound having the structure :*

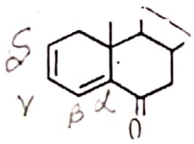


Solution. The given compound is an α, β-unsaturated six-membered ring ketone. It has one ring residue at α-position and two at β-positions and has double bonds exocyclic to two rings as shown below :

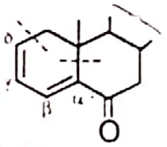


∴ Parent value for α, β-unsaturated 6 membered cyclic ketone		= 215 nm
One ring residue at α-position		= 10 nm
Two ring residues at β-position,	2 × 12	= 24 nm
Double bond exocyclic to two rings	2 × 5	= 10 nm
∴ **Calculated value**		= **259 nm**
Observed value		= **256 nm**

Example 1.11. *Compute* λ_{max} *for the structure :*



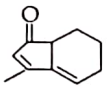
Solution. The given structure represents an α, β-unsaturated six membered ring ketone having a ring residue at α-position and another ring residue at δ-position. It has an exocyclic double bond, a double bond extending conjugation and a homoannular diene component.



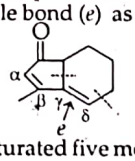
Parent value		= 215 nm
One α-ring residue		= 10 nm

One δ ring residue	= 18 nm
One exocyclic double bond	= 5 nm
One double bond extending conjugation	= 30 nm
One homoannular conjugated diene	= 39 nm
∴ **Calculated value**	= **317 nm**
Observed value	= **319 nm**

Example 1.12. *Calculate λ_{max} for the following compound :*

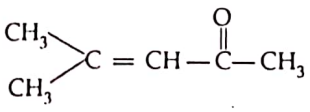


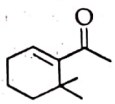
Solution. The given compound is a α, β-unsaturated five membered ring ketone having a methyl group at β-position, a ring residue at γ-position, a ring residue at δ-position, a double bond extending conjugation and an exocyclic double bond (*e*) as shown below.



∴ Parent value for α, β-unsaturated five membered cyclic ketone	= 202 nm
One alkyl substituent at β-position	= 12 nm
One ring residue at γ-position	= 18 nm
One ring residue at δ-position	= 18 nm
One exocyclic double bond	= 5 nm
One double bond extending conjugation	= 30 nm
∴ **Calculated value**	= **285 nm**
Observed value	= **287 nm**

Problem 1.8. *On the basis of Woodward-Fieser rules, calculate λ_{max} for the following compounds :*

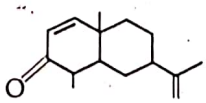
(*i*) 

(ii) 

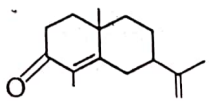
Ans. (*i*) Parent α, β-unsaturated acyclic ketone (215 nm) + 2 β-alkyl substituents (2 × 12 = 24 nm) = 239 nm

(*ii*) Parent value (215 nm) + One α ring residue (10 nm) + β ring residue (12 nm) + β–alkyl substituent (12 nm) = 249 nm]

Problem 1.9. *A given compound is expected to have the structure either A or B. Its UV spectrum shows λ_{max} at 252 nm. Predict its actual structure.*



(A)



(B)

[**Ans.** Calculate λ_{max} for both A and B. (A = 215 + 12 for β ring residue = 227; B = 215 + 10 for alkyl group at α-position + 2 × 12 for 2 β ring residues + 5 for exocyclic double bond = 254).
The actual structure is B.]