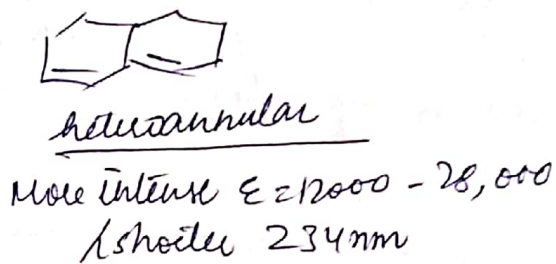
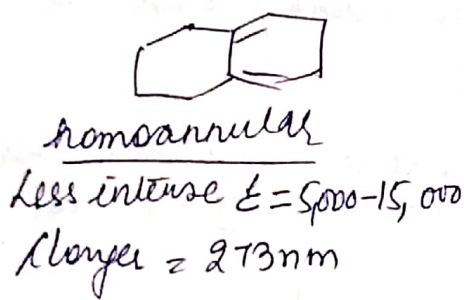
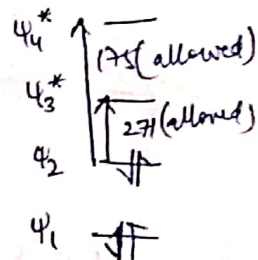
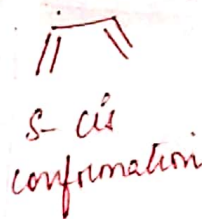
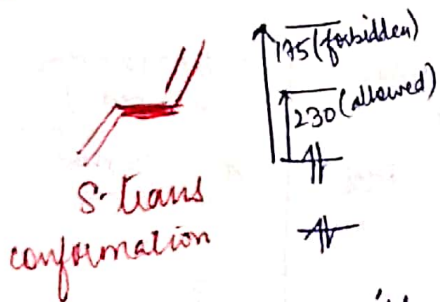


Woodward Fischer Rule

- ⇒ By studying a vast number of diene, Woodward and Fischer devised an empirical correlation of structural variations that enable us to predict the wavelength at which a conjugated diene will absorb.
- ⇒ determine the λ_{max} value for dienes
- ⇒ Woodward Fischer rule for dienes is either homoannular with both double bonds contained in one ring or heteroannular with 2 double bonds distributed b/w 2 rings.

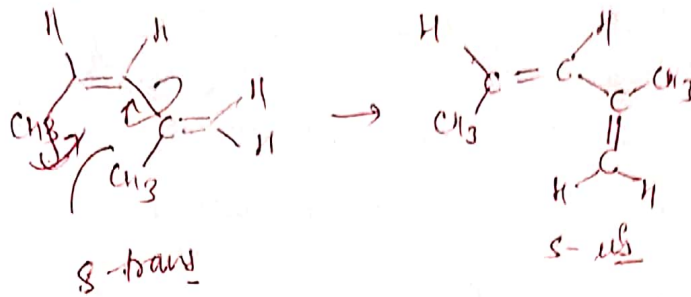


Imp



- ⇒ In butadiene, 2 possible $\pi \rightarrow \pi^*$ transitions occur
 $\psi_2 \rightarrow \psi_3^*$ & $\psi_2 \rightarrow \psi_4^*$.
- ⇒ $\psi_2 \rightarrow \psi_4^*$ transition is not often observed; it lies near 175 nm & it is forbidden transition for s-trans conformation of double bonds in butadiene.
- ⇒ A transition at 175 nm lies below the cutoff points of the common solvent used to determine UV spectra and therefore is not easily detectable. s-trans conformation is more favorable than s-cis conformation. Therefore 175 nm band is not usually determined.

⇒ conjugated dienes exhibit an intense band ($\epsilon = 20,000$ to $26,000$) in region from 217 to 245 nm owing to $\pi \rightarrow \pi^*$ transition (quite intense)



Imp ⇒ conjugated diene exist in $s\text{-trans}$ and $s\text{-cis}$ conformation.

⇒ The 1,3-dialkylbutadienes possess too much crowding b/w alkyl group to permit them to exist in the $s\text{-trans}$ conformation. They convert, by rotation around the single bond to an $s\text{-cis}$ conformation, which absorbs at longer wavelength but with lower intensity than the corresponding $s\text{-trans}$ conformation.

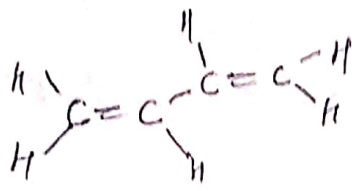
⇒ In cyclic dienes, where the central bond is a part of the ring system the diene chromophore is either $s\text{-trans}$ (transoid) or the $s\text{-cis}$ (cisoid) orientation.

1) homoannular (cisoid or $s\text{-cis}$)

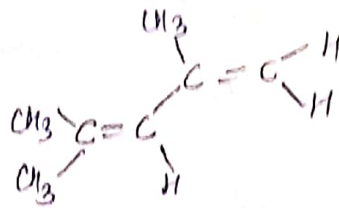
2) heteroannular (transoid or $s\text{-trans}$)

Empirical Rules for dienes:

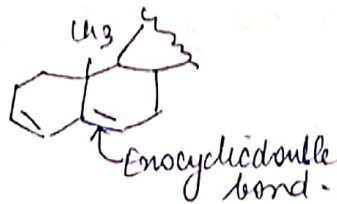
	homoannular (cisoid)	heteroannular (transoid)
Parent	$\lambda_{max} = 253\text{nm}$	$\lambda = 214\text{nm}$
Increament for:-		
Double bond extend conjugation	30	30
Alkyl substituent or ring residue	5	5
exocyclic double bond	5	5
polare grouping:-		
-COCH ₃	0	0
-OR	6	6
-Cl, -Br	5	5
-NR ₂	60	60



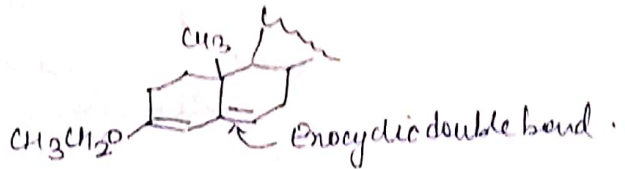
Transoid = 214nm
observed = 217nm.



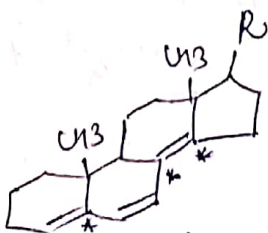
Transoid = 214nm
alkyl groups = 3x5 = 15
229nm
observed = 228nm.



Transoid 214nm
Ring residue 3x5 15
Exocyclic double bond 5
234nm
observed 235nm

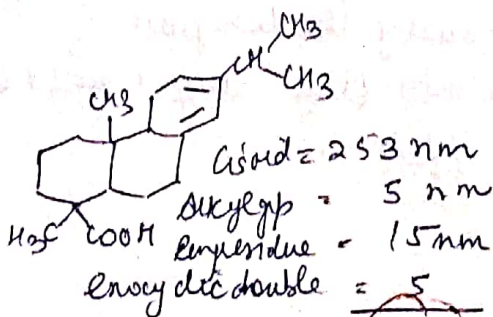


Transoid 214nm
Ring residue 3x5 15
Exocyclic -OR 5
240nm
observed 241nm

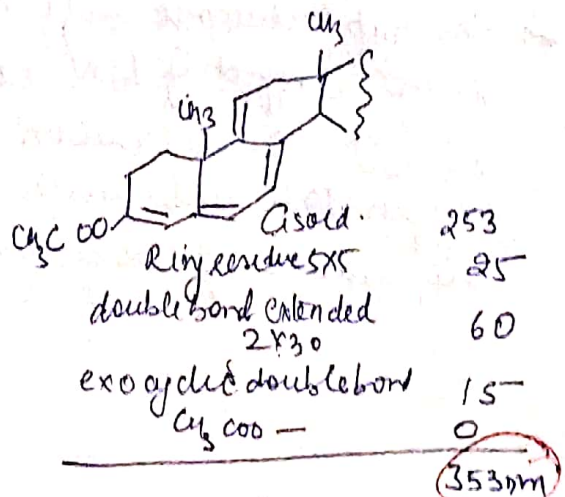


Three Exocyclic double bonds = 3x5 = 15nm

Exocyclic double bond: It is a double bond that lies outside of a given ring.
⇒ Exocyclic may lie within the ring even though it is outside another ring.
⇒ an exocyclic double bond will be found at a junction point on rings.



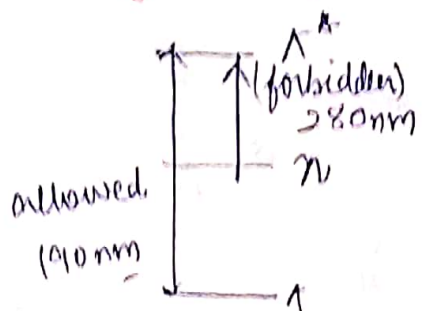
Asoid = 253nm
alkyl gp = 5nm
Ring residue = 15nm
Exocyclic double = 5
278
observed = 275nm



Asoid 253
Ring residue 5x5 25
double bond extended 2x30 60
exocyclic double bond 15
CH₃COO - 0
353nm

observed = 275nm
Scanned with CamScanner

⇒ Carbonyl compounds: Enone:



$n \rightarrow \pi^*$ transition although it is (weak) (weak due to forbidden) is commonly observed in carbonyl compounds -

⇒ Substitution on the carbonyl grp by an auxochrome with a lone pair of e^- such as $-NR_2, -OH, -OR, -NH_2$ or $-X$ as in amide, acids ester, or acid chlorides gives a pronounced hypsochromic effect on the $n \rightarrow \pi^*$ transition and a lesser bathochromic effect on the $\pi \rightarrow \pi^*$ transition.

↓
caused by resonance interaction

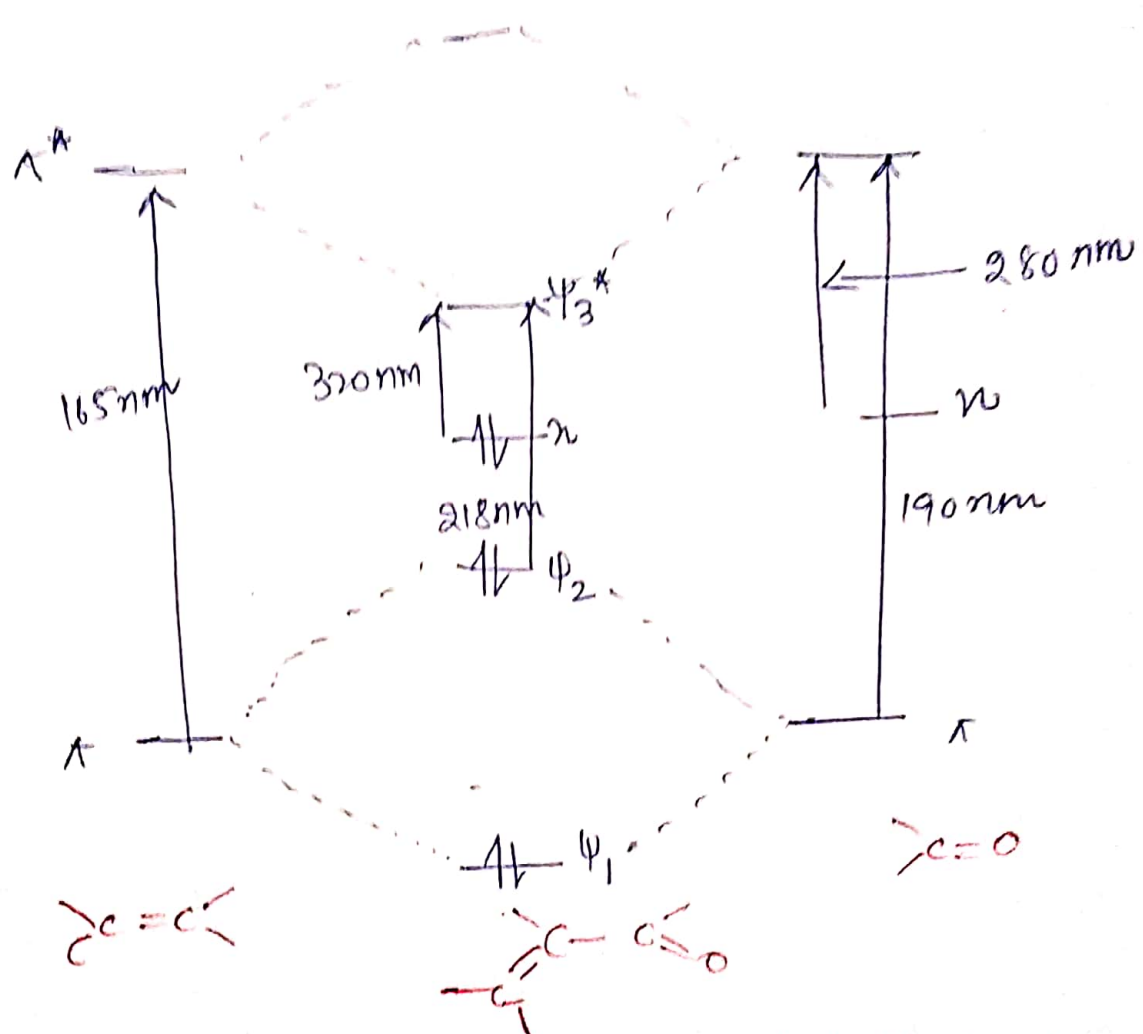
	λ_{max}	ϵ_{max}
$CH_3-C(=O)-H$	293	12
$CH_3-C(=O)-CH_3$	279	15 max
$CH_3-C(=O)-Cl$	235	53
$CH_3-C(=O)-NH_2$	214	-
$CH_3-C(=O)-OCH_2CH_3$	204	60
$CH_3-C(=O)-OH$	204	41

← hypsochromic effect of lone pair auxochromes on the $n \rightarrow \pi^*$ transition of a carbonyl group.

⇒ The hypsochromic shift of the $n \rightarrow \pi^*$ is due primarily to the +I effect of O, N & halogen atoms. They withdraw e^- from $>C=O$ carbon, causing the lone pair of e^- on oxygen to be held more firmly than they would be in the absence of inductive effect.

→ If the carbonyl group is part of conjugated system of double bonds, both $n \rightarrow \pi^*$ & $\pi \rightarrow \pi^*$, shifted to longer λ . However the energy of $n \rightarrow \pi^*$ doesn't decrease as quickly as that of $\pi \rightarrow \pi^*$, which is more intense.

→ If the conjugated chain becomes long enough the $n \rightarrow \pi^*$ band is buried under the more intense $\pi \rightarrow \pi^*$ band -



⇒ orbital of enone system compared to those of non-interacting chromophores