UV-Visible Spectroscopy

Prediction of λ_{max}: For Alkene

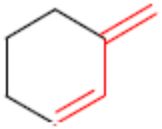
Woodward-Fieser Rules:

For an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ transition

A base value for λ_{max} of the chromophore:

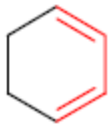
acyclic (*s*-trans)

214



transoid

214



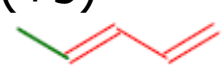
cisoid

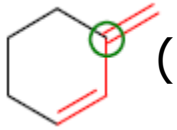
253

The incremental contribution of substituents is added to this base value from the group tables:

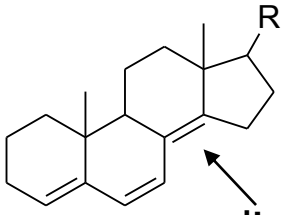
(+30)

(+5)





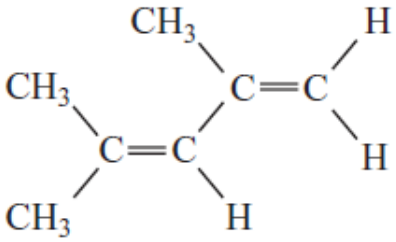
(+5)



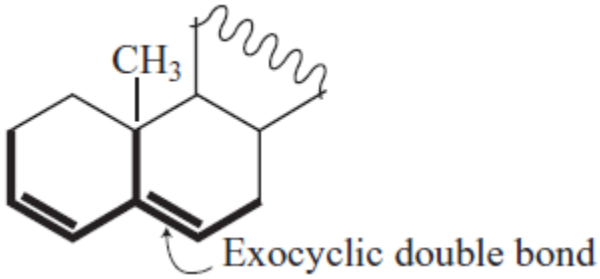
exocyclic to two rings

Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
$-OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
$-NR_2$	+60

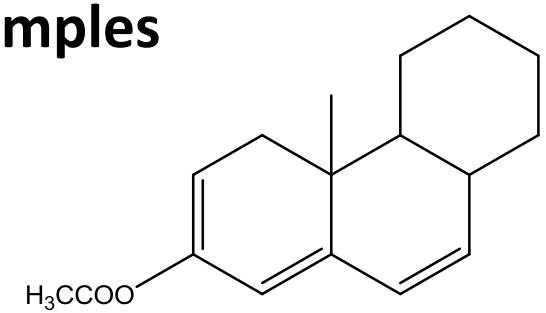
Prediction of λ_{max}: Examples



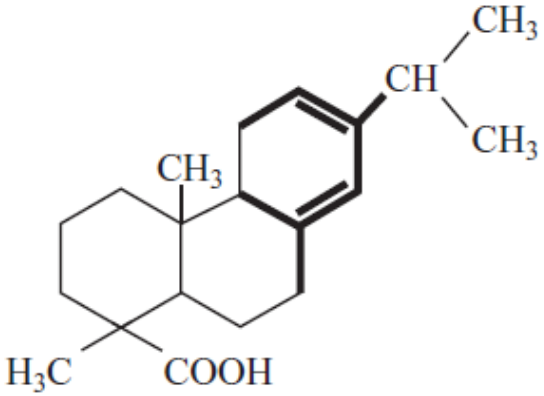
Transoid:	214 nm
Alkyl groups: 3 × 5 =	15
	229 nm
Observed:	228 nm



Transoid:	214 nm
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
	234 nm
Observed:	235 nm

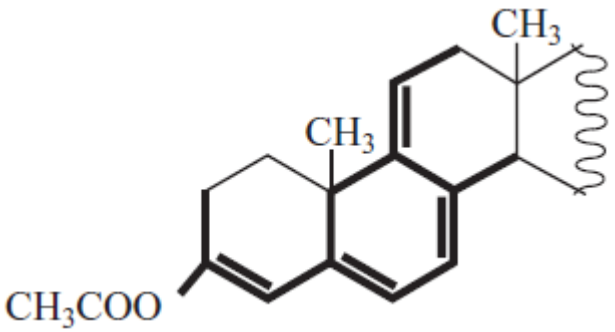


Homoanular diene	253 nm
Extra conjugation	30 nm
one exocyclic C=C	+ 5 nm
3 alkyl subs.	+15 nm
	303 nm
Experimental value	306 nm



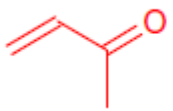
Cisoid:	253 nm
Alkyl substituent:	5
Ring residues: 3 × 5 =	15
Exocyclic double bond:	5
	278 nm
Observed:	275 nm

Prediction of λ_{max}: Examples



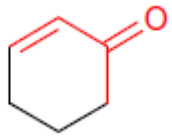
Observed: 355 nm

Prediction of λ_{max}: For Unsturated Ketone



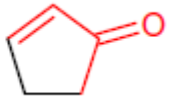
acyclic (*s*-trans)

215



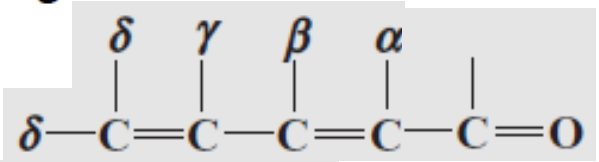
6-membered ring

215

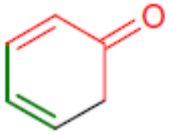


5-membered ring

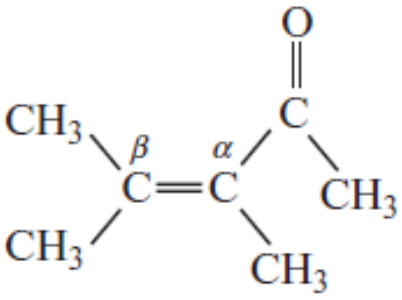
202



Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18



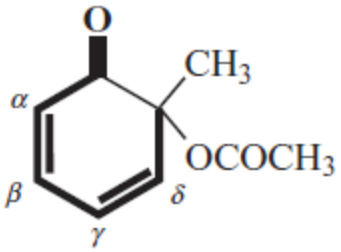
homocyclic (cisoid) diene 39



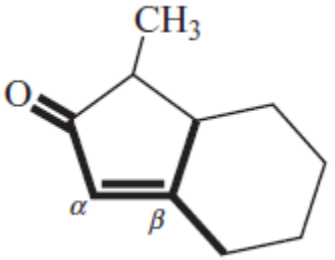
Acyclic enone:	215 nm
α-CH_3:	10
β-CH_3: $2 \times 12 =$	24
	249 nm
Observed:	249 nm

Polar groupings:		
$-OH$	α	35
	β	30
	δ	50
$-OCOCH_3$	α,β,δ	6
$-OCH_3$	α	35
	β	30
	γ	17
	δ	31
$-Cl$	α	15
	β	12
$-Br$	α	25
	β	30
$-NR_2$	β	95
Exocyclic double bond		5

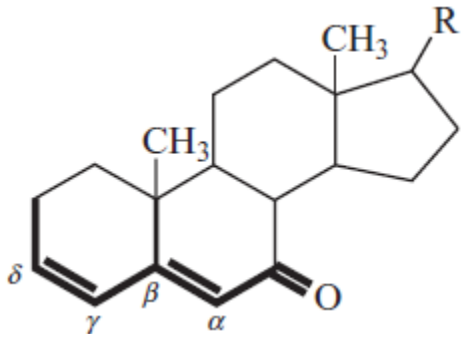
Prediction of λ_{max}: For Unsturated Ketone



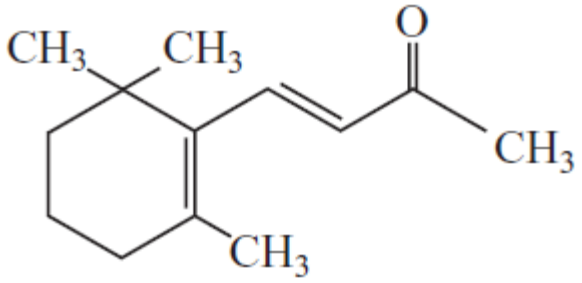
Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
Homocyclic diene:	39
δ-Ring residue:	18
	302 nm
Observed:	300 nm



Five-membered enone:	202 nm
β-Ring residue: $2 \times 12 =$	24
Exocyclic double bond:	5
	231 nm
Observed:	226 nm



Six-membered enone:	215 nm
Double-bond-extending conjugation:	30
β-Ring residue:	12
δ-Ring residue:	18
Exocyclic double bond:	5
	280 nm
Observed:	280 nm



Woodward-Fieser Rules is not valid for conjugation with more than four double bonds

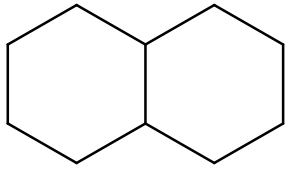
Summary and Problem

Bands of high intensity that appear above 210 nm generally represent either an unsaturated ketone, a diene, or a polyene.

*Simple ketones, acids, esters, amides, and other compounds containing both p systems and unshared electron pairs show two absorptions: an **n** to **π*** transition at longer wavelengths* (>300 nm, low intensity) and a **π to π*** transition at shorter wavelengths (<250 nm, high intensity).

With conjugation (enones), the λ_{max} of the **π to π*** band moves to longer wavelengths and can be predicted by Woodward's Rules.

A compound with the molecular formula of $C_{10}H_{14}$ has the basic skeleton as shown below. Provide the exact molecular structure of the compound, if the λ_{max} for the compound is 234 nm.

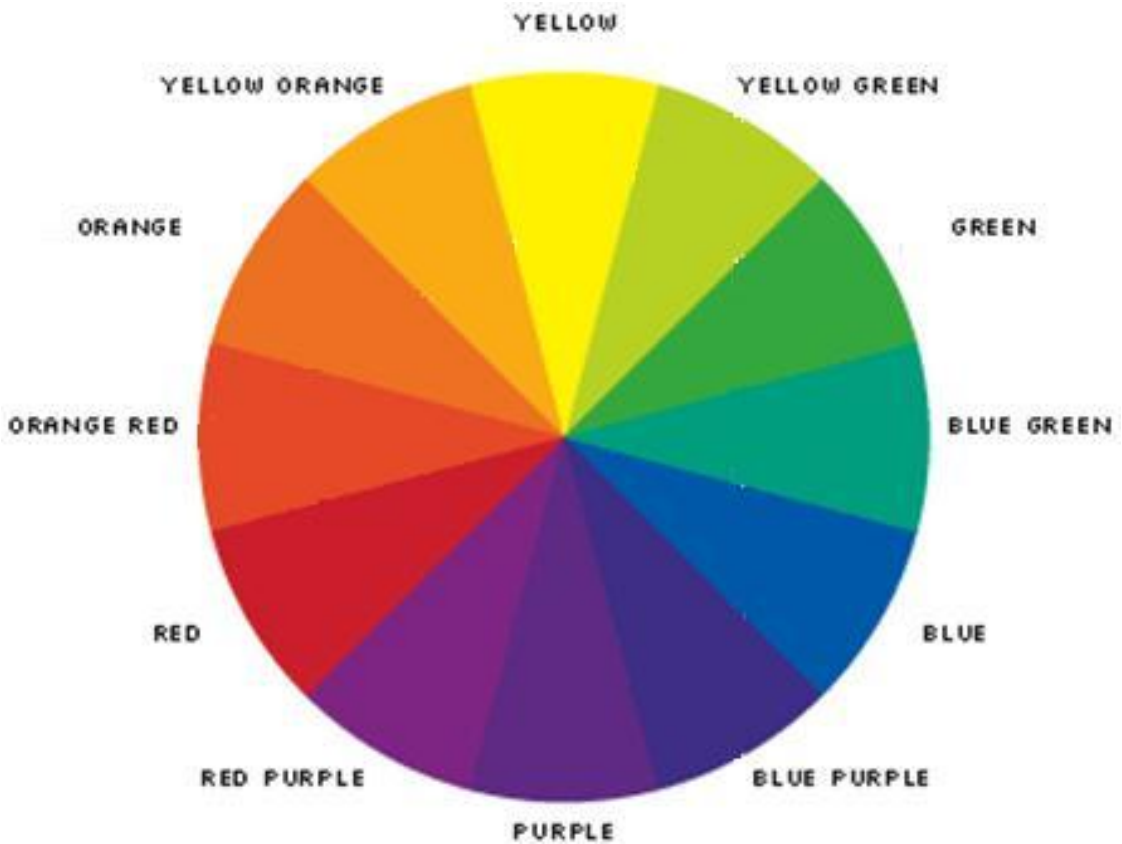


VISIBLE SPECTRA: COLOR OF COMPOUNDS

electromagnetic spectrum lying between about 400 and 750 nm is the **visible** region
Light waves with wavelengths between these limits appear colored to the human eye

If a substance absorbs visible light, it appears to have a color; if not, it appears white

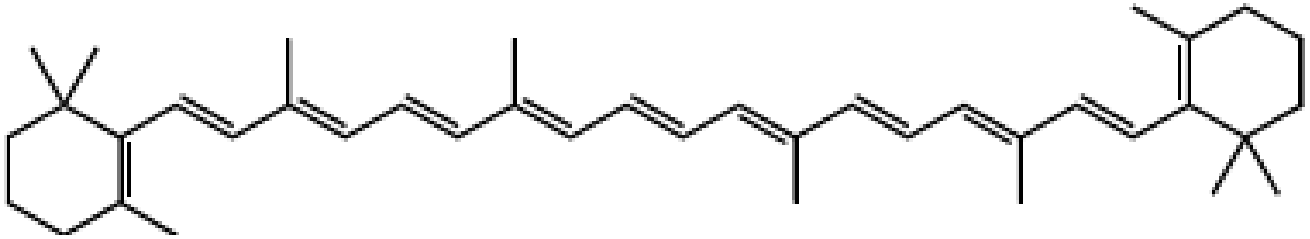
compounds that absorb light in the visible region of the spectrum do not possess the color corresponding to the wavelength of the absorbed light



Compounds show **complementary** color

Absorbed color	λ_{abs}	Observed color
Violet	400	Yellow
Blue	450	Orange
Blue-green	500	Red
Yellow-green	530	Red-violet
Yellow	550	Violet
Orange-red	600	Blue-green
Red	700	Green

VISIBLE SPECTRA: COLOR OF COMPOUNDS



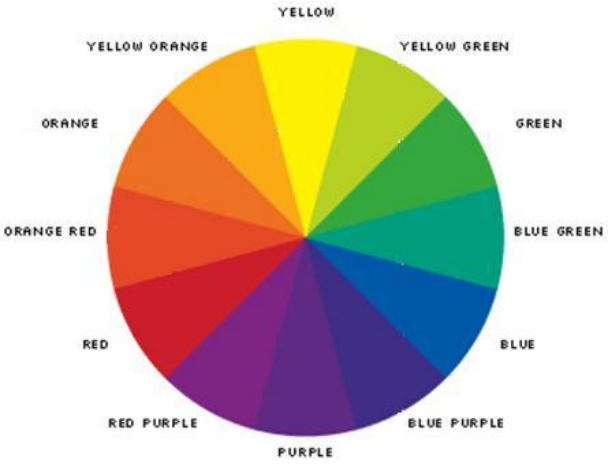
β-carotene, λ_{max} = 455 nm (Blue region)

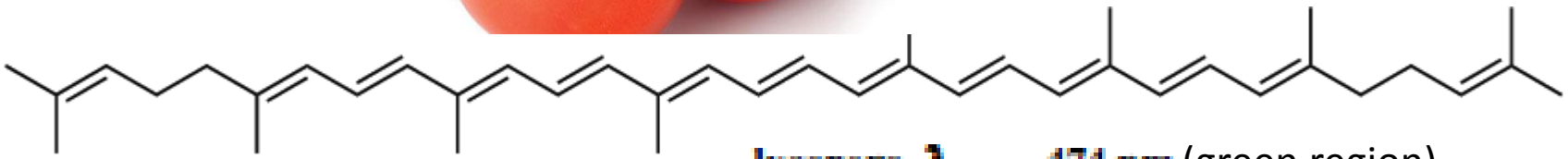
λ_{max} = 114 + 5(# alkyl substituents) + n(48 - 1.7n) - 16.5(# endo) - 10(# exo)

= 114 + 5(10) + 11(48 - 1.7•11) - 16.5(2) - 0

= 453.3 nm

Fieser-Kuhn Rules



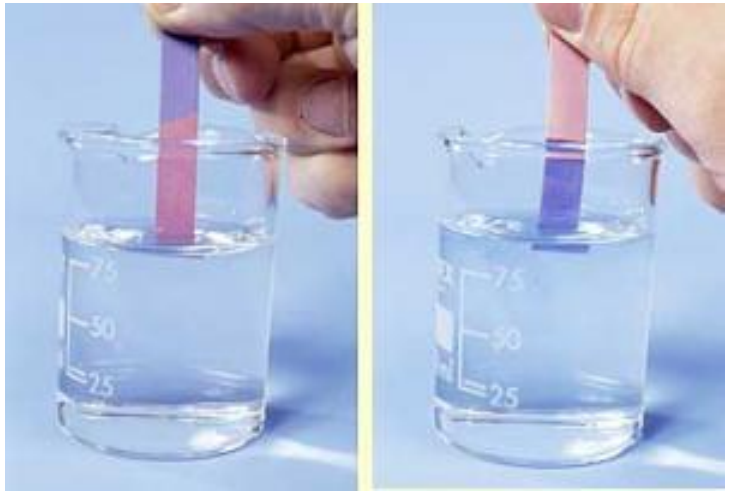


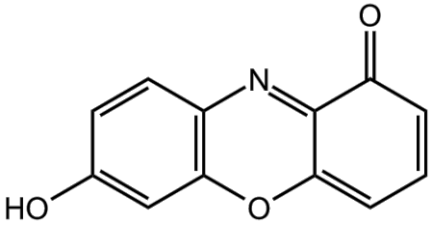
lycopene, λ_{max} = 474 nm (green region)

λ_{max} = 114 + 5(8) + 11(48 - 1.7•11) - 0 - 0

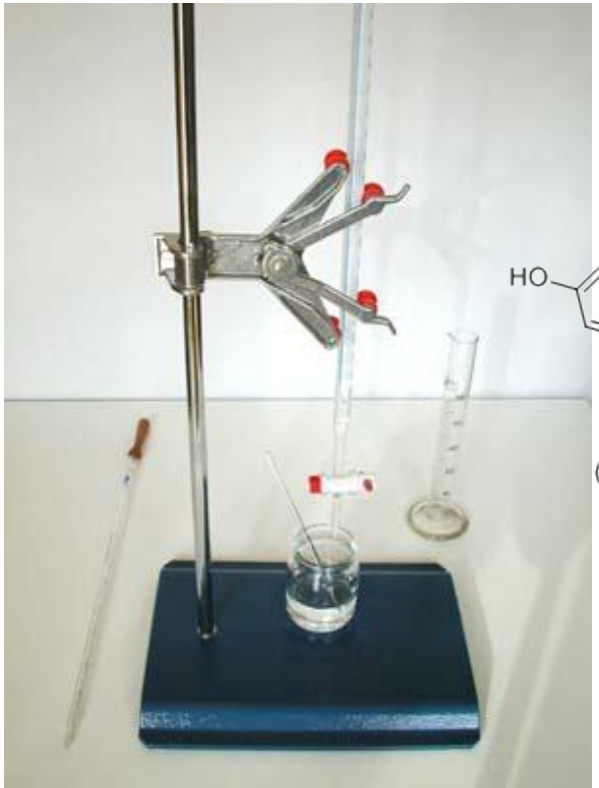
= 476 nm

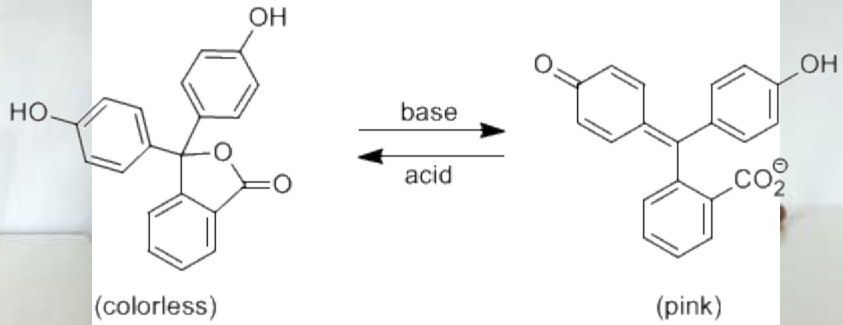
VISIBLE SPECTRA: COLOR OF COMPOUNDS



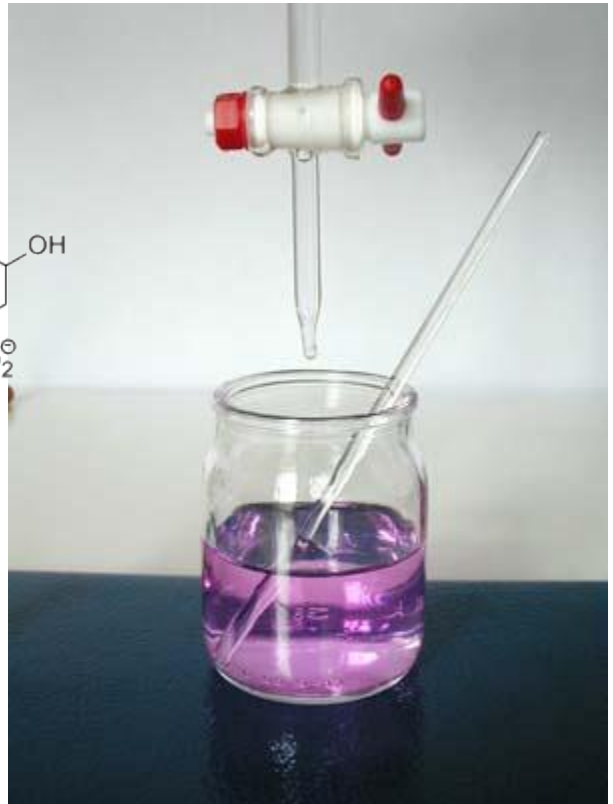


7-hydroxyphenoxazone





(colorless) (pink)



Problem

A cyclic carbonyl compound **A** with molecular formula of C_5H_6O. It shows a strong absorption at 214 nm. If a hydrogen is replaced by a CH_3 group, the λ_{max} shifted to 226 nm. Provide the exact molecular structure of the compound **A**, and the compound with λ_{max} =226.

Looking forward

IR and NMR spectroscopy

Course material will be uploaded **after 17:00** h on **every Friday**@

http://www.iitg.ac.in/ckjana/ckjana/Teaching.html