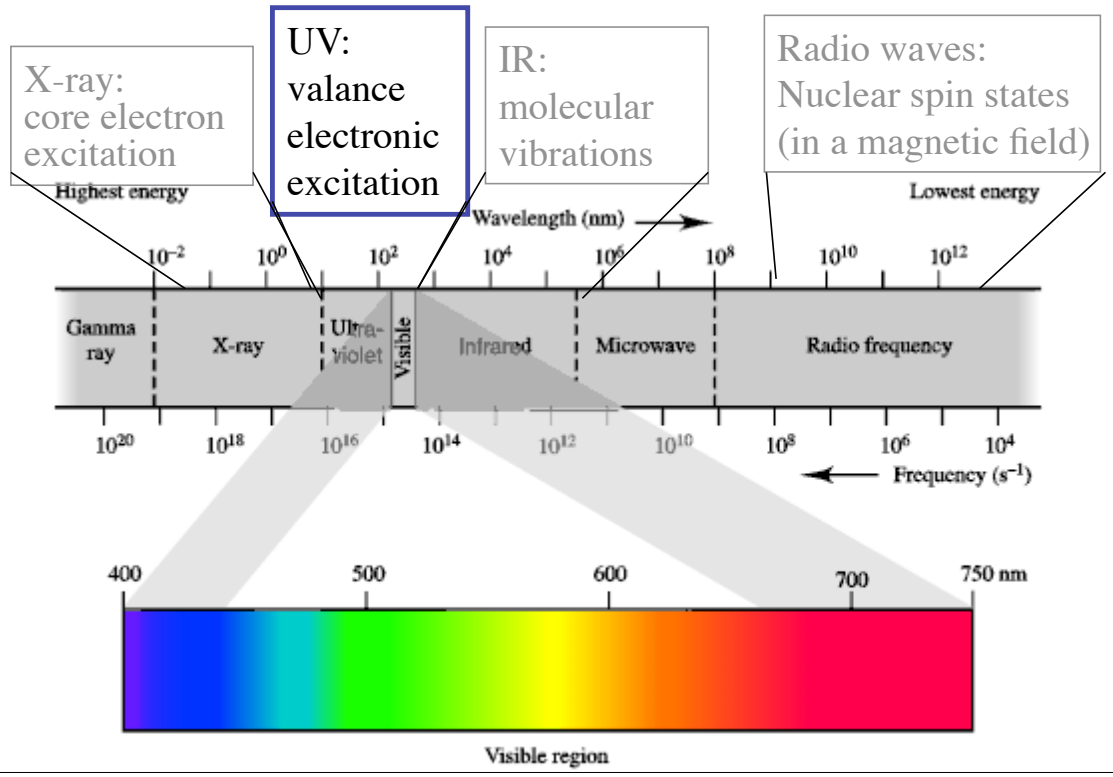
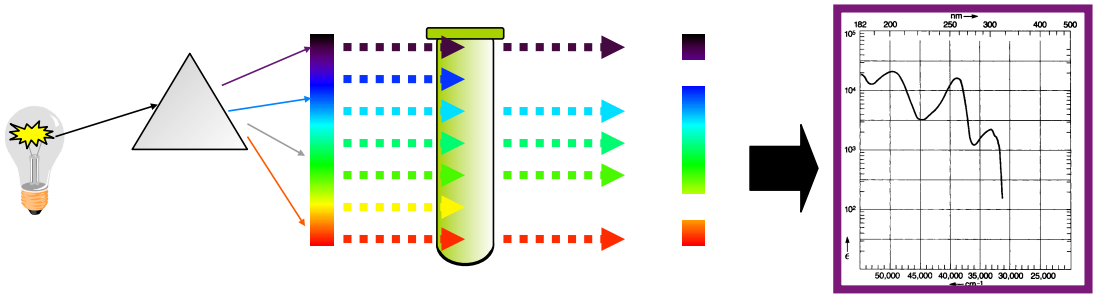
Electronic Excitation by UV/Vis Spectroscopy :





The wavelength and amount of light that a compound absorbs depends on its molecular structure and the concentration of the compound used.

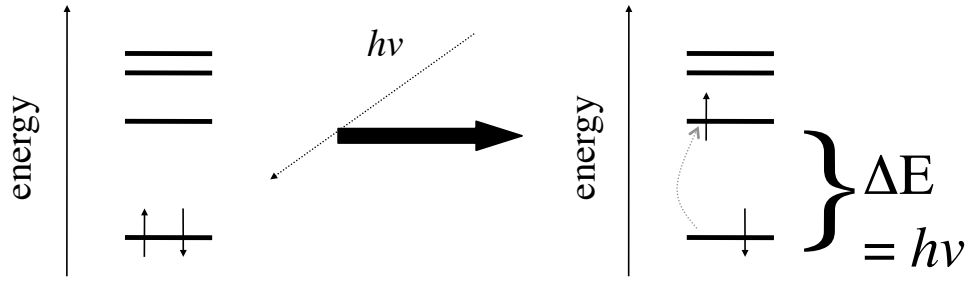
The concentration dependence follows Beer's Law.

$$A = \varepsilon bc$$

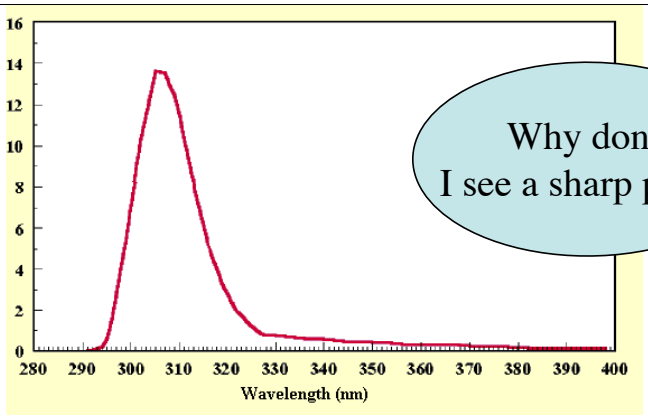
Where A is absorbance (no units, since $A = log10\ P0 / P$)
ε is the molar absorbtivity with units of L mol-1 cm-1
b is the path length of the sample - that is, the path length of the cuvette in which the sample is contained (typically in cm).
c is the concentration of the compound in solution, expressed in mol L-1

Molecules have quantized energy levels:

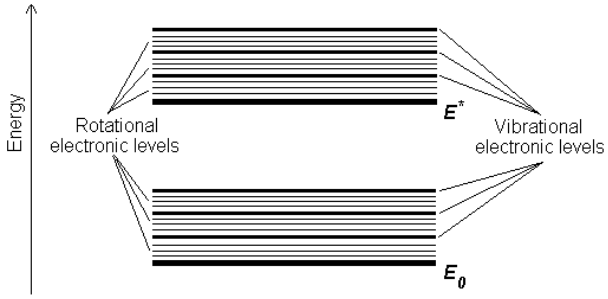
ex. electronic energy levels.

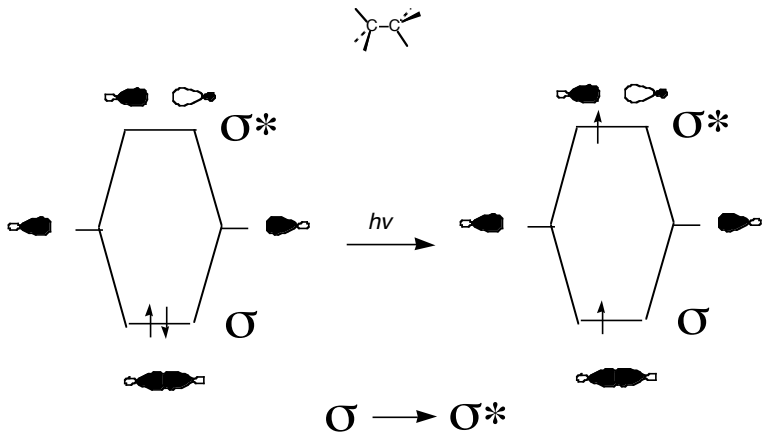


Q: Where do these quantized energy levels come from?
A: The electronic configurations of associated with bonding.



Each electronic energy level (configuration) has associated with it the many vibrational and rotational energy levels we examined with IR.

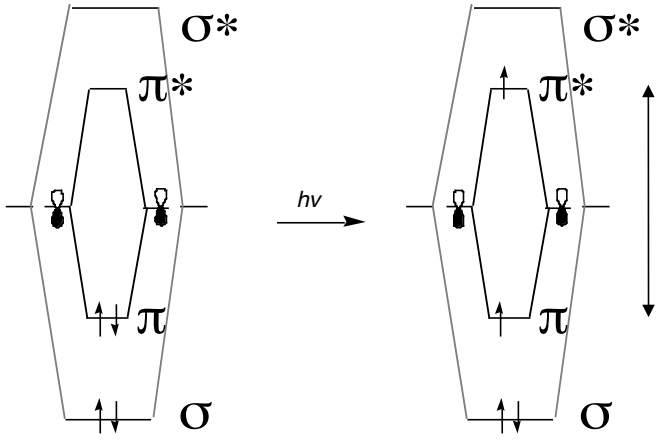




$\sigma \longrightarrow \sigma^*$

λ_{max} = 135 nm (a high energy transition)

Absorptions having λ_{max} < 200 nm are difficult to observe because everything (including quartz glass and air) absorbs in this spectral region.

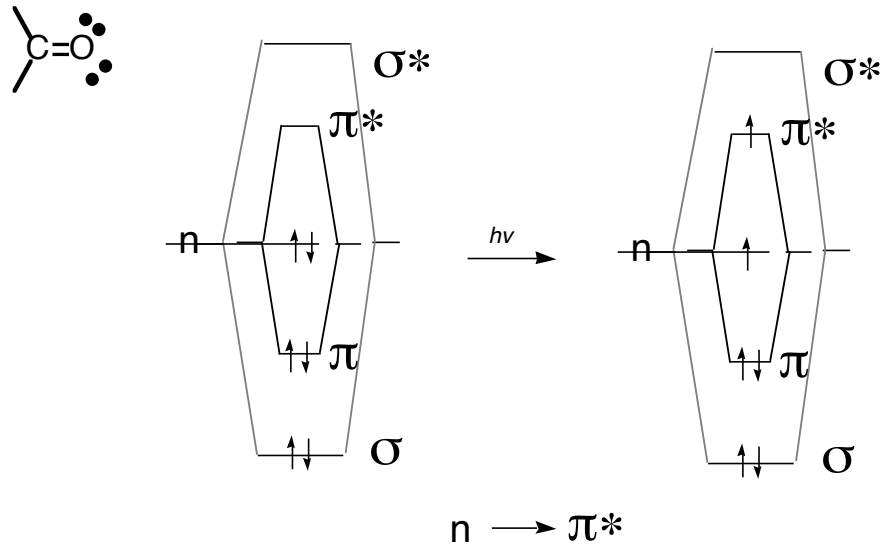


$\Delta E = h\nu = hc/\lambda$

$\pi \longrightarrow \pi^*$

Example: ethylene absorbs at longer wavelengths:

λ_{max} = 165 nm ε= 10,000



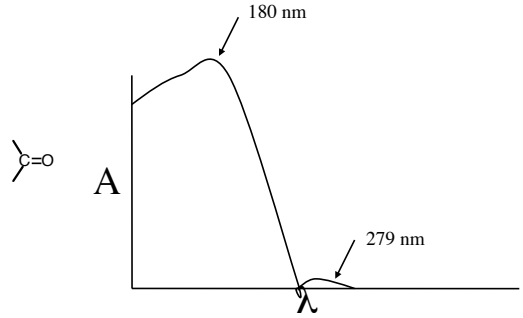
Example:

Acetone: n–σ* λ_{max} = 188 nm ; ε= 1860

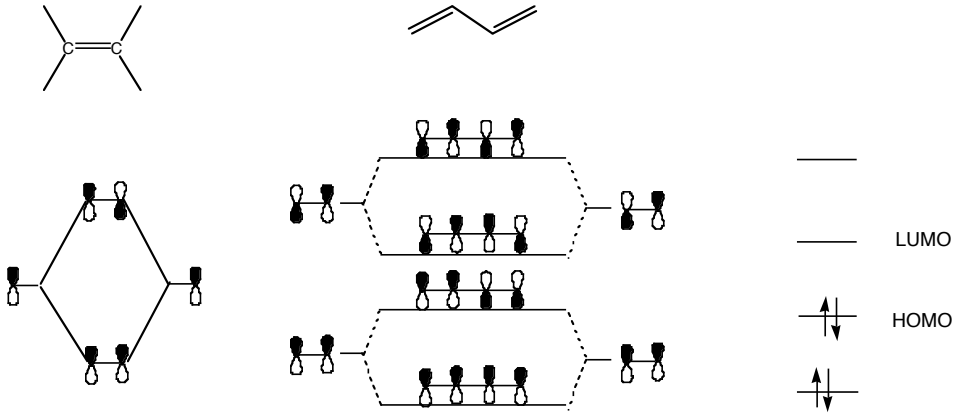
n–π* λ_{max} = 279 nm ; ε= 15

Summary:

C–C	σ –> σ*	135 nm	
C=C	π –> π*	165 nm	
C=O	π –> π*	150 nm	
	n –> σ*	188 nm	
	n –> π*	279 nm	weak



Conjugated systems:



Preferred transition is between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

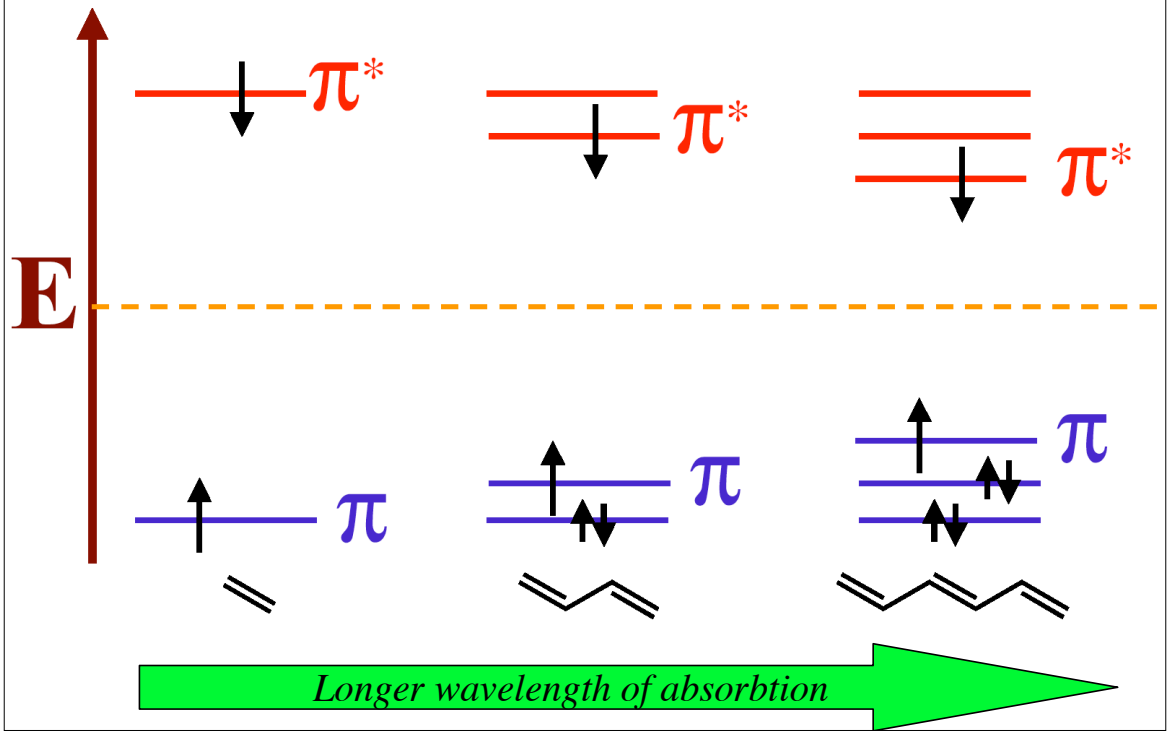
Note: Additional conjugation (double bonds) lowers the HOMO-LUMO energy gap:

Example:

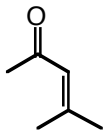
1,3 butadiene: λ_{max} = 217 nm ; ε= 21,000

1,3,5-hexatriene λ_{max} = 258 nm ; ε= 35,000

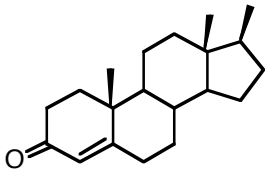
π-π* excitation in polyenes



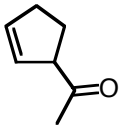
Similar structures have similar UV spectra:



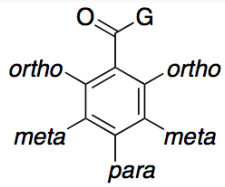
λ_{max} = 238, 305 nm



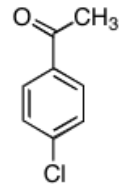
λ_{max} = 240, 311 nm



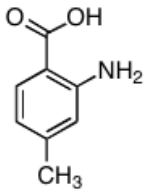
λ_{max} = 173, 192 nm



ArCOR/ArCHO/$ArCO_2H$/$ArCO_2R$		λ_{max}^{EtOH} (nm)
Parent chromophore: Ar = C_6H_5		
G = Alkyl or ring residue, (e.g., ArCOR)		246
G = H, (ArCHO)		250
G = OH, OAlk, ($ArCO_2H$ and $ArCO_2R$)		230
Increment for each substituent on Ar:		
—Alkyl or ring residue	o-, m-	+3
	p-	+10
—OH, —OCH_3, —OAlk	o-, m-	+7
	p-	+25
—O^- (oxyanion)	o-	+11
	m-	+20
	p-	+78[b]
—Cl	o-, m-	+0
	p-	+10
—Br	o-, m-	+2
	p-	+15
—NH_2	o-, m-	+13
	p-	+58
—$NHCOCH_3$	o-, m-	+20
	p-	+45
—$NHCH_3$	p-	+73
—$N(CH_3)_2$	o-, m-	+20
	p-	+85

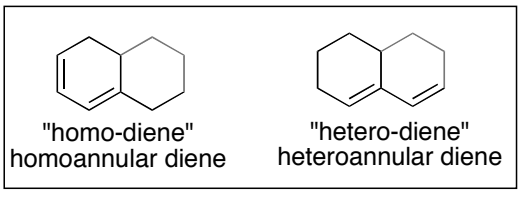


base: 246
p-Cl: +10
256



base: 230
p-CH_3: +10
o-NH_2: +13
253

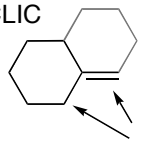
UV-VIS Calculation Tables: Dienes



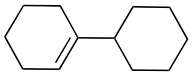
"homo-diene"
homoannular diene

"hetero-diene"
heteroannular diene

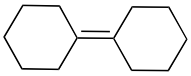
EXOCYCLIC



Double bond has an atom that is part of a ring that the other is not.

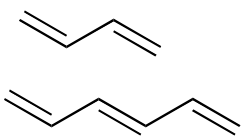


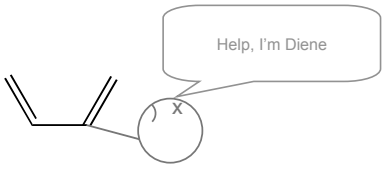
NOT EXOCYCLIC



2-exocyclic components

UV-VIS Calculation Tables: Dienes





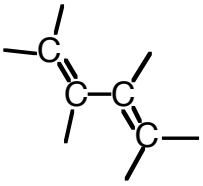
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

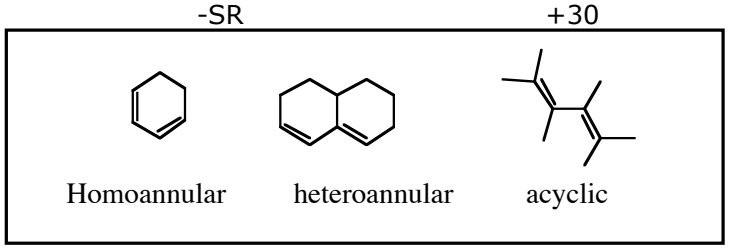
[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, 63, 1123 (1941); 64, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

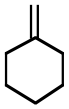
[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

Woodward-Fieser Rules for Dienes

	Homoannular	Heteroannular
Parent	λ=253 nm	λ=214 nm =217 (acyclic)
Increments for:		
Double bond extending conjugation	+30	
Alkyl substituent or ring residue		+5
Exocyclic double bond		+5
Polar groupings:		
-OC(O)CH3		+0
-OR		+6
-Cl, -Br		+5
-NR2		+60
-SR		+30



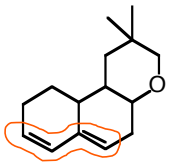




exocyclic

For more than 4 conjugated double bonds:

$\lambda_{max} = 114 + 5(\#\text{ of alkyl groups}) + n(48.0\text{-}1.7n)$



Parent: 214 (heteroannular)

3 alkyls +15 (3x5)

+5 (exocyclic)

TOTAL 234 nm

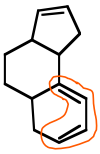
(Actual = 235 nm)

TABLE 7.5

Rules of Diene Absorption[a]	
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5 x3
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.



Parent: 253 (homoannular)

3 alkyls +15 (3x5)

+5 (exocyclic)

TOTAL 273 nm

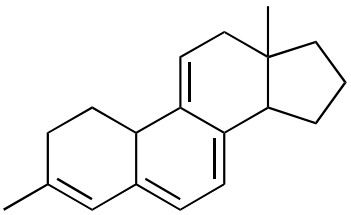
(Actual = 275 nm)

TABLE 7.5

Rules of Diene Absorption[a]	
Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5 x3
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.



Base(homodiene)
253

2 DBE	60
6 alkyls	30
3 exocyclic olefins	15
	358 nm

TABLE 7.5

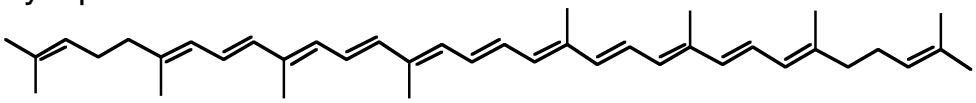
Rules of Diene Absorption[a]

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
λ_{calc} = Total	

[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold, 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*. New York: Pergamon (Macmillan), 1964.

[b]Solvents have negligible effects upon the λ_{max} of these $\pi \rightarrow \pi^*$ transitions.

Lycopene:

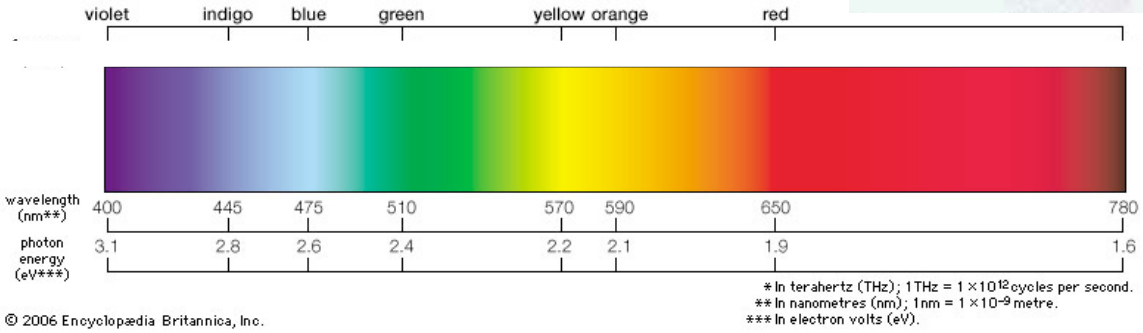


For more than 4 conjugated double bonds:
λ_{max} = 114 + 5(# of alkyl groups) + n(48.0-1.7n)

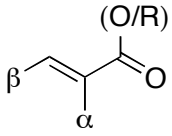
λ_{max} = 114 + 5(8) + 11*(48.0-1.7*11) = 476 nm

λ_{max}(Actual) = 474.

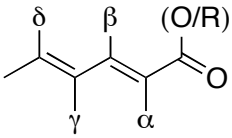
Light, the visible spectrum



*In terahertz (THz); 1THz = 1×10^{12} cycles per second.
**In nanometres (nm); 1nm = 1×10^{-9} metre.
***In electron volts (eV).



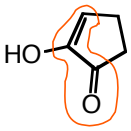
enone



dienone

Base values		(nm)
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
—NR_2	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]

[a]Two conjugated double bonds, both in the same ring.
[b]The calculated values usually fall within ±3 nm of the observed values. The molar absorptivities of *cisoid* enones are usually less than 10,000, whereas the molar absorptivities of *transoid* enones are greater than 10,000.



Parent: 202 (5-member ring ketone)

+35 (alpha hydroxyl)

+12 (beta alkyl - note part of ring)

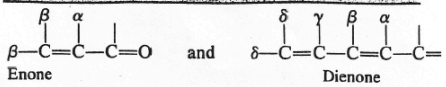
Total: 249

Note: Carbonyl substitution is implicitly included in calculation as designated by parent "ketone", "ester", "aldehyde"….

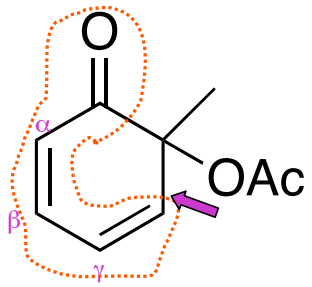
Do not add an addition subsitution for this group!

TABLE 7.12

Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyl Compounds)



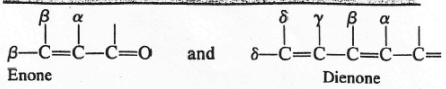
Base values		(nm)
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
—NR_2	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]



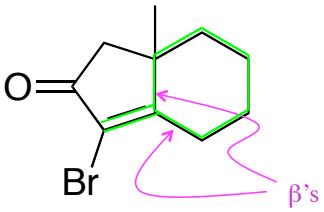
Base		215
Double bond extension(DBE)		30
δ alkyl		18
homodiene		39
		302 nm

TABLE 7.12

Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyl Compounds)



		(nm)
Base values		
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
$—NR_2$	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]

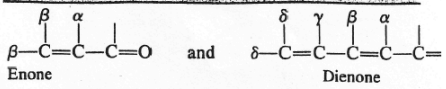


Base (5 member ring)		202
α bromo		25
2 β alkyls		24
Exocyclic olefin		5
		256 nm

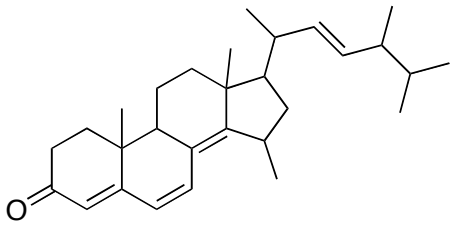
2 x

TABLE 7.12

Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyl Compounds)



		(nm)
Base values		
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
$—NR_2$	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]

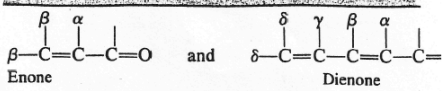


Base	215	
2 DBE	60	
βalkyl		12
3 >γ alkyl	39	
3 exocyclic olefins	15	

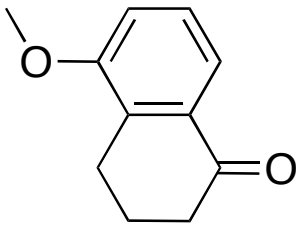
356 nm

TABLE 7.12

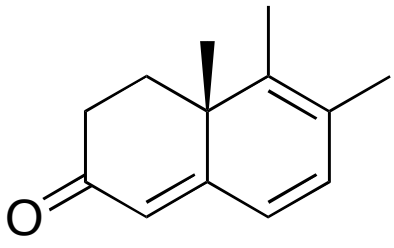
Rules of Enone and Dienone Absorption (α,β-Unsaturated Carbonyl Compounds)



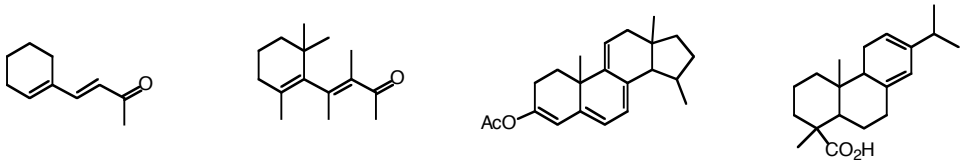
		(nm)
Base values		
Acyclic α,β-unsaturated ketones		215
Six-membered cyclic α,β-unsaturated ketones		215
Five-membered cyclic α,β-unsaturated ketones		202
α,β-Unsaturated aldehydes		210
α,β-Unsaturated carboxylic acids and esters		195
Increments for		
Double bond extending conjugation		+30
Alkyl group, ring residue	α	+10
	β	+12
	γ and higher	+18
Polar groupings: —OH	α	+35
	β	+30
	δ	+50
—OAc	α,β,δ	+ 6
—OMe	α	+35
	β	+30
	γ	+17
	δ	+31
—SAlk	β	+85
—Cl	α	+15
	β	+12
—Br	α	+25
	β	+30
$-NR_2$	β	+95
Exocyclic double bond		+5
Homodiene component[a]		+39
Solvent correction (see table below)		Variable
		λ_{calc} = Total[b]



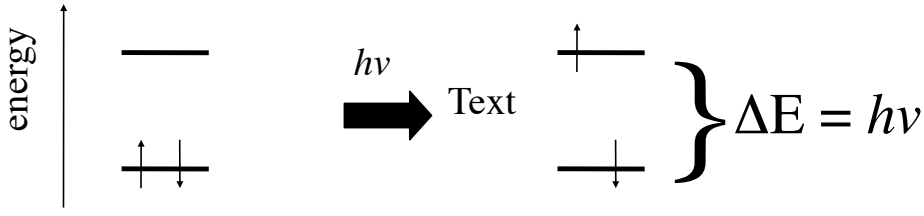
exp = 276 nm



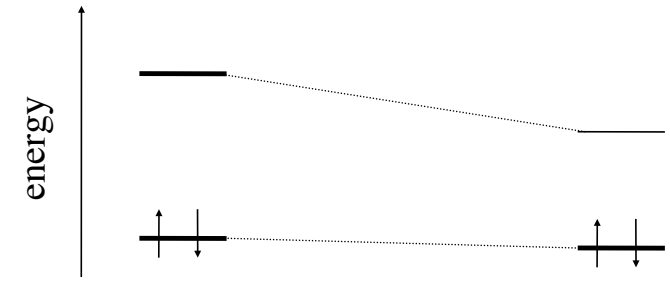
exp = 388 nm

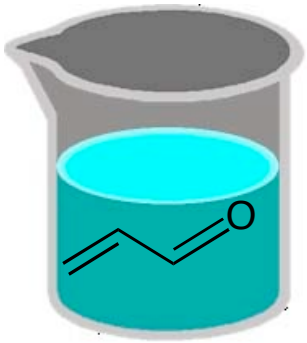


What do excited states look like?

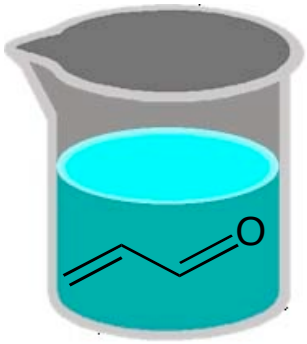


Why should I care?





In Hexane



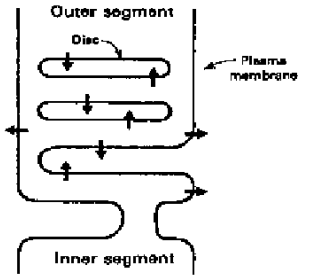
In Methanol

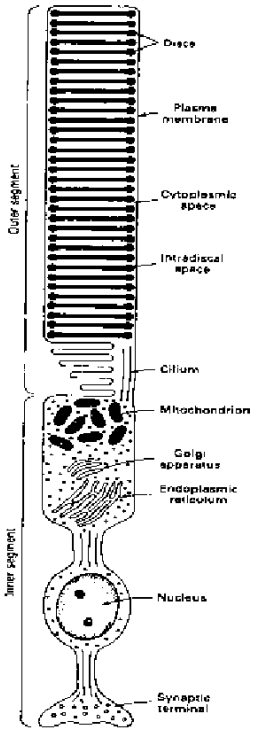
RED-shifted

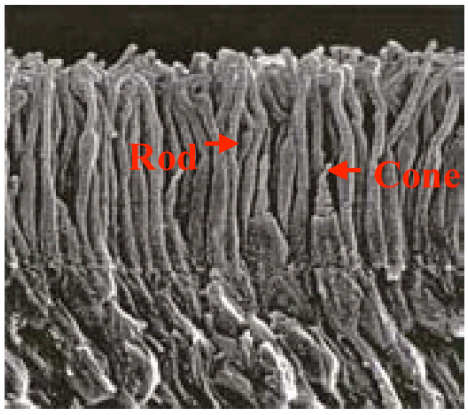
Visual Receptors

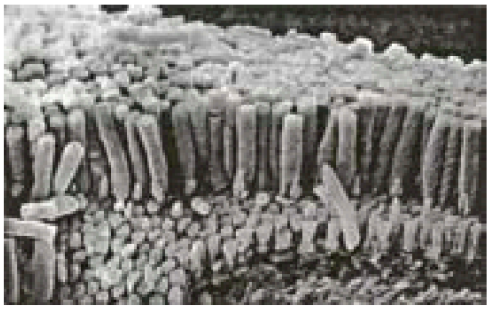
Light

G-protein signaling pathway









Rhodopsin

Visual Receptors

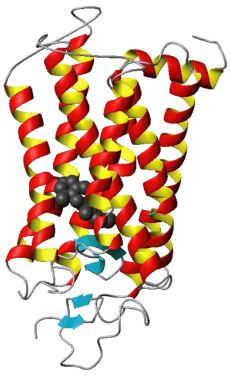
Light

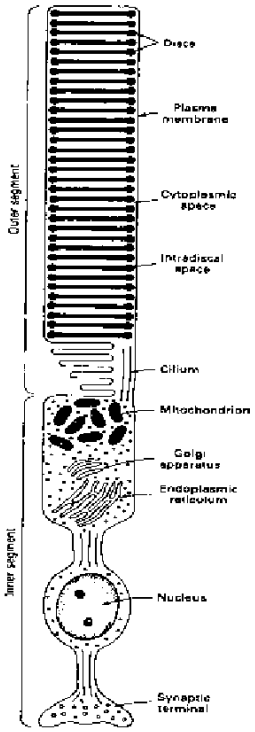
• **photoreceptor cell**, is a specialized type of neuron (nerve cell) found in the eye's retina that is capable of phototransduction.

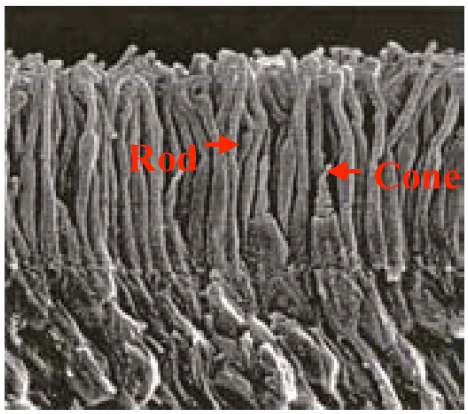
• **rod and cone cells:**
photoreceptor cells in the retina of the eye

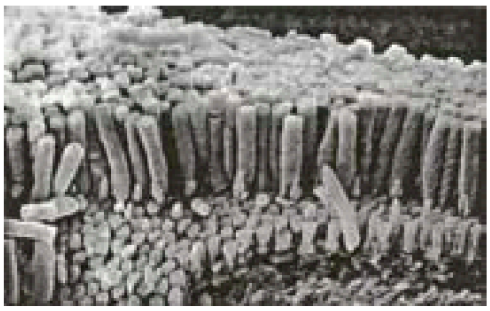
• There are about 90 million rod cells in the human retina.

• Rhodopsin: key integral membrane protein

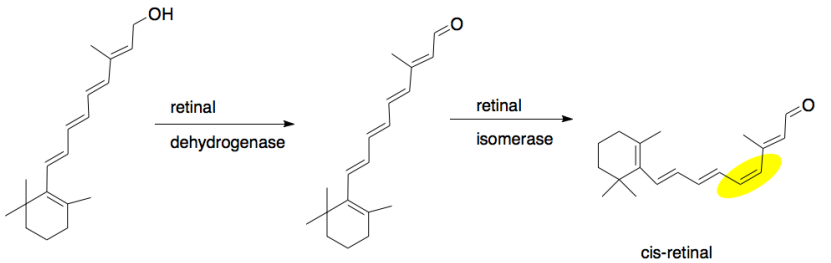


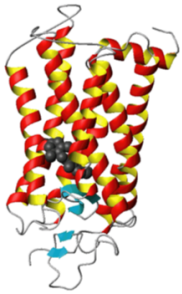




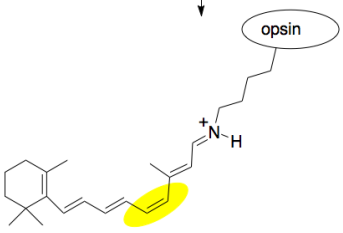


Eat your carrots

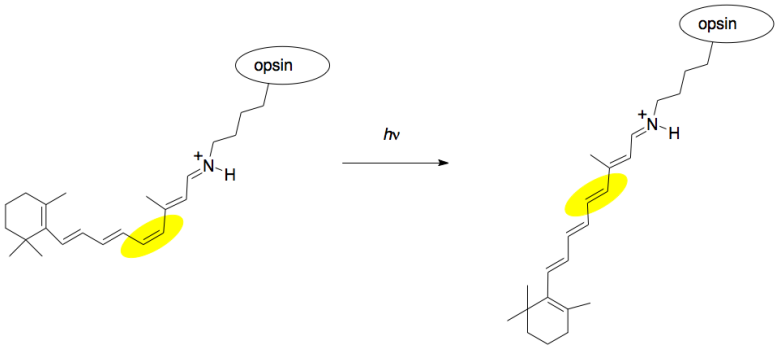




"rhodopsin" =
opsin (the protein)
+ trans-retinal



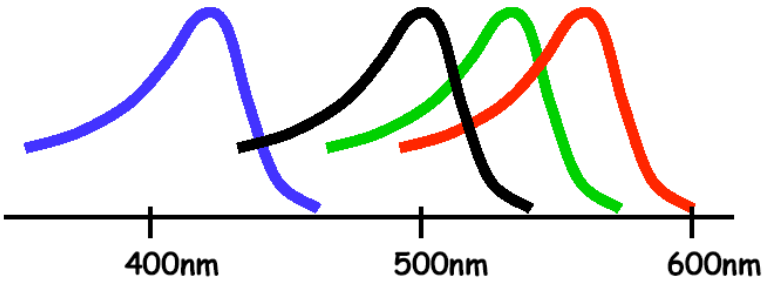
chemistry of vision



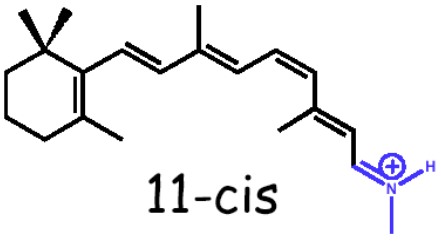
Absorption of light causes a cis-trans isomerization

structural change and subsequent hydrolysis triggers an enzymatic cascade, leading to closure of cation specific channels in the plasma membrane. This blocks the influx of Na ions and leads to hyper polarization of the membrane. This sends a signal to the synapse.

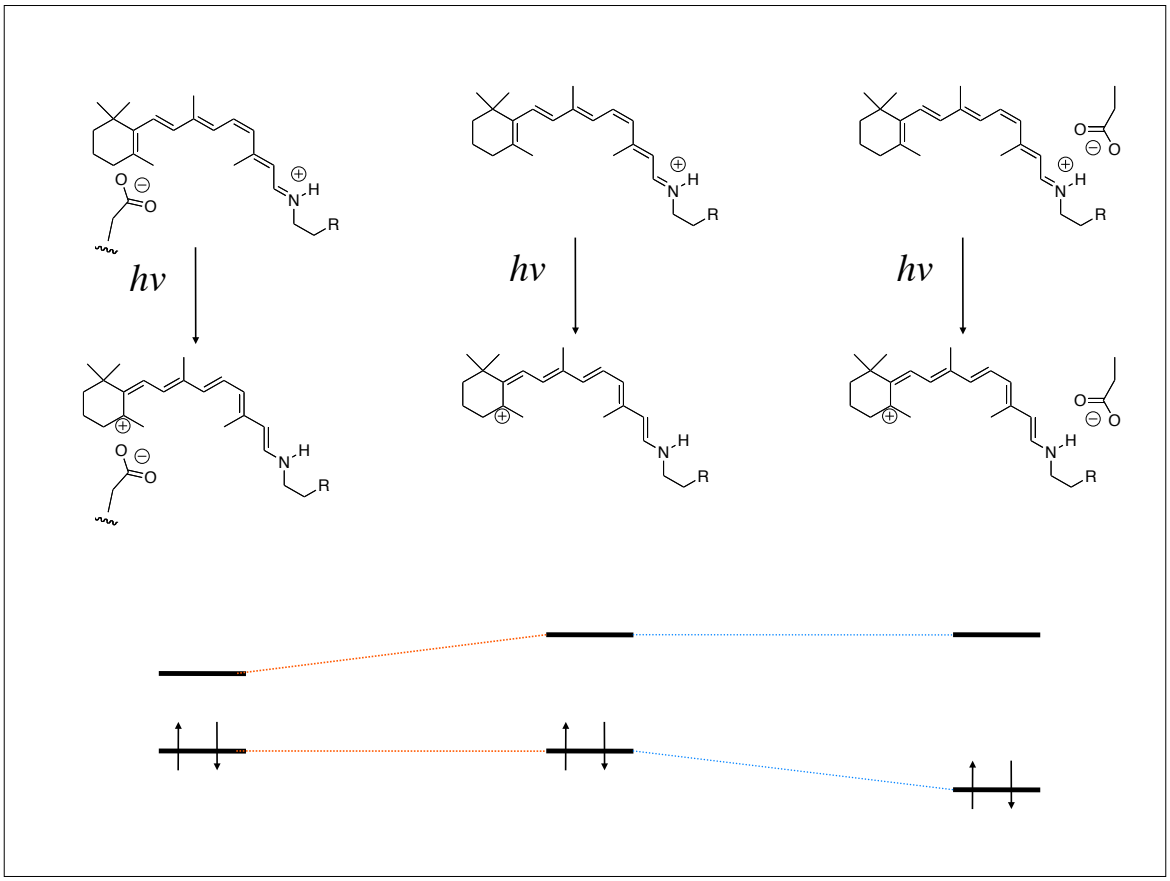
Color is sensed by red, green and blue rhodopsin visual receptors.



absorption spectrum



Their chromophores are exactly the same!


hv
hv
hv