UV-VIS spectroscopy
or
Electronic Spectroscopy (Part-II-B)

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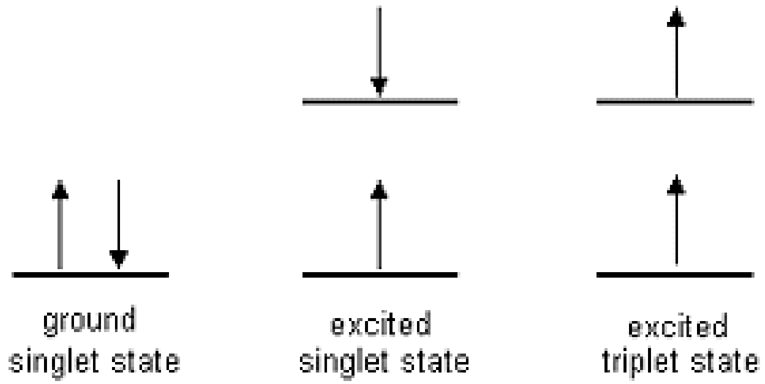
More Complex Electronic Processes

- **Fluorescence:** absorption of radiation to an excited state, followed by emission of radiation to a lower state of the same multiplicity (singlet to singlet transition.)
- **Phosphorescence:** absorption of radiation to an excited state, followed by emission of radiation to a lower state of different multiplicity (triplet to singlet transition
- **Singlet state:** spins are paired, no net angular momentum (and no net magnetic field)
- **Triplet state:** spins are unpaired, net angular momentum (and net magnetic field)

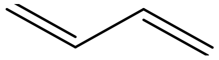


IV. Structure Determination

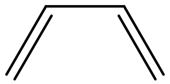
A. Dienes

1. General Features

For acyclic butadiene, two conformers are possible – *s-cis* and *s-trans*



s-trans



s-cis

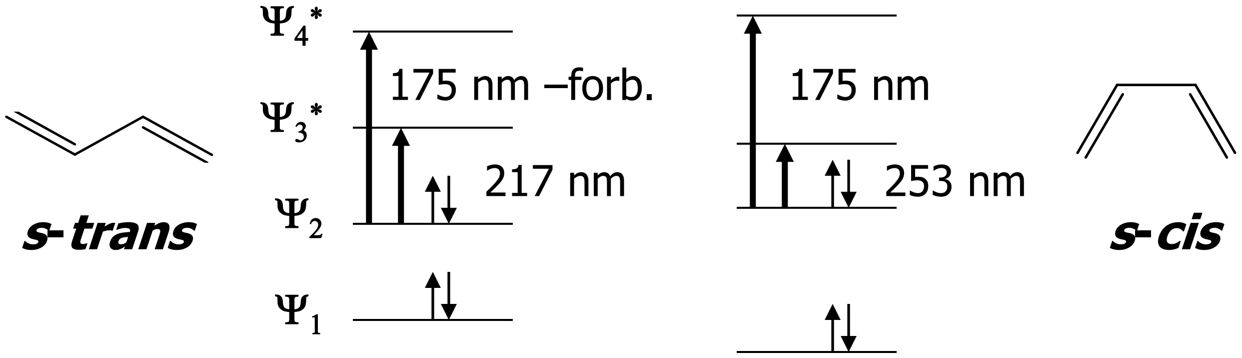
The *s-cis* conformer is at an overall higher potential energy than the *s-trans*; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength

Structure Determination

A. Dienes

1. General Features

Two possible $\pi \rightarrow \pi^*$ transitions can occur for butadiene $\Psi_2 \rightarrow \Psi_3^*$ and $\Psi_2 \rightarrow \Psi_4^*$



The $\Psi_2 \rightarrow \Psi_4^*$ transition is not typically observed:

- The energy of this transition places it outside the region typically observed – 175 nm
- For the more favorable *s-trans* conformation, this transition is forbidden

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption

Structure Determination

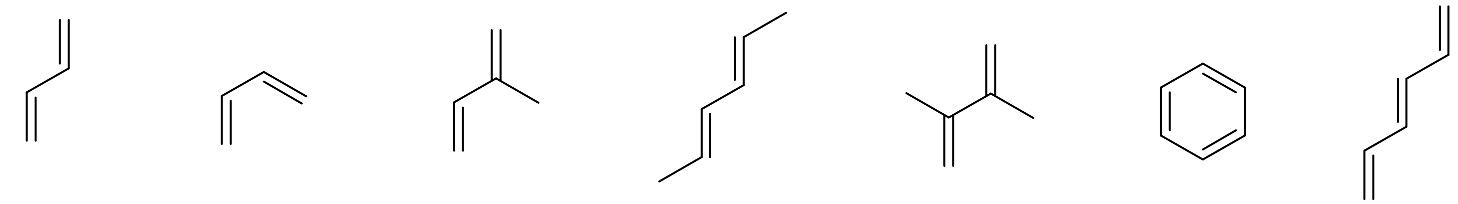
A. Dienes

1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption (e = 20,000+) based at 217 nm within the observed region of the UV

While this band is insensitive to solvent (as would be expected) it is subject to the bathochromic and hyperchromic effects of alkyl substituents as well as further conjugation

Consider:



λ_{max} = 217 253 220 227 227 256 263 nm

Structure Determination

A. Dienes

2. Woodward-Fieser Rules

Woodward and the Fiesers performed extensive studies of terpene and steroidal alkenes and noted similar substituents and structural features would predictably lead to an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ electronic transition

This work was distilled by Scott in 1964 into an extensive treatise on the Woodward-Fieser rules in combination with comprehensive tables and examples – (A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon, NY, 1964)

A more modern interpretation was compiled by Rao in 1975 – (C.N.R. Rao, *Ultraviolet and Visible Spectroscopy*, 3rd Ed., Butterworths, London, 1975)

Dienes

2. Woodward-Fieser Rules - Dienes

The rules begin with a base value for λ_{max} of the chromophore being observed:

acyclic butadiene = 214 nm

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

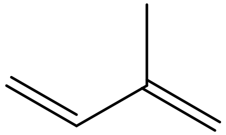
Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
-$OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR_2	+60

Structure Determination

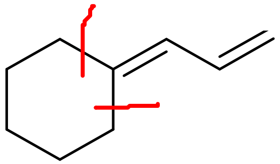
A. Dienes

2. Woodward-Fieser Rules - Dienes

For example:



Isoprene - acyclic butadiene =	214 nm
one alkyl subs.	+ 5 nm
	219 nm
Experimental value	220 nm



Allylidenecyclohexane

- acyclic butadiene =	214 nm
one exocyclic C=C	+ 5 nm
2 alkyl subs.	+10 nm
	229 nm
Experimental value	237 nm

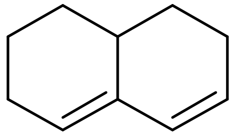
Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

There are two major types of cyclic dienes, with two different base values

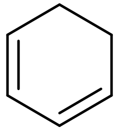
Heteroannular (transoid):



ε = 5,000 – 15,000

base λ_{max} = 214

Homoannular (cisoid):



ε = 12,000-28,000

base λ_{max} = 253

The increment table is the same as for acyclic butadienes with a couple additions:

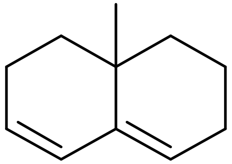
Group	Increment
Additional homoannular	+39
Where both types of diene are present, the one with the longer λ becomes the base	

Structure Determination

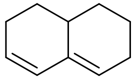
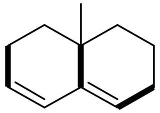
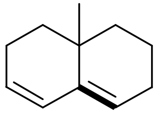
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

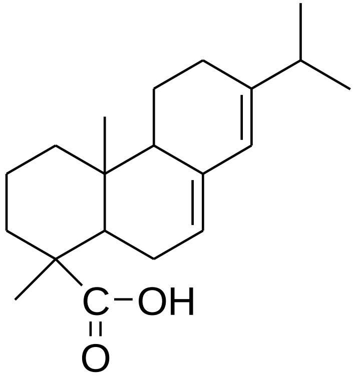
For example:



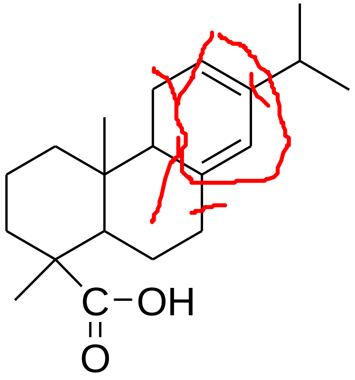
1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene

	heteroannular diene =	214 nm
	3 alkyl subs. (3 x 5)	+15 nm
	1 exo C=C	+ 5 nm
		234 nm
	Experimental value	235 nm

IV. Structure Determination
A. Dienes
3. Woodward-Fieser Rules – Cyclic Dienes



heteroannular diene =	214 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
	239 nm



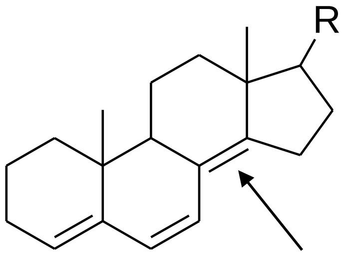
homoannular diene =	253 nm
4 alkyl subs. (4 x 5)	+20 nm
1 exo C=C	+ 5 nm
	278 nm

Structure Determination

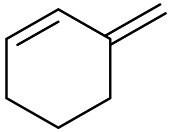
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

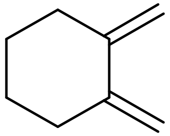
Be careful with your assignments – three common errors:



This compound has three exocyclic double bonds; the indicated bond is exocyclic to ***two*** rings



This is ***not*** a heteroannular diene; you would use the base value for an acyclic diene



Likewise, this is ***not*** a homooannular diene; you would use the base value for an acyclic diene

Base value = 214

Exocyclic double bond = 5, Ring residue 2×5 = 10

λ_{max} = 229 nm.

5.

Base value = 253 nm

D.B.Ex con = 30 "

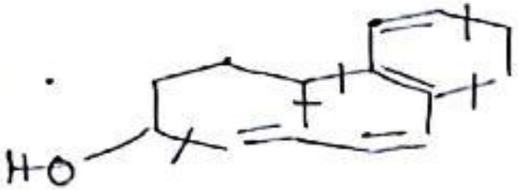
Exocyclic D.B = 5 "

Ring residue = 15 (5×3) "

Polar gr = 6 "

λ_{max} 309 nm

6.



Base value = 253 nm

2 D.B.E. = 60 "

Ring residue(5) = 25 "

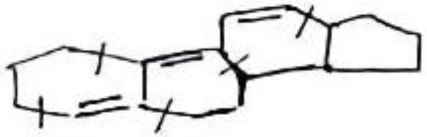
Exocyclic double bond = 5 "

λ_{max} = 343 nm

7.

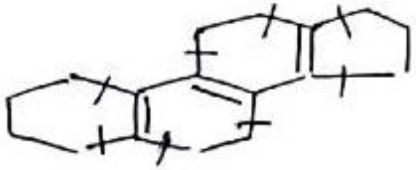
Base value = 253 nm
Ex. D.B (2×5) = 10 "
D.B. Ex Conj = 30 "
Ring Resid. = 20 "
λ_{max} 313 "

8.



→ B.V = 214 "
Ring Residue = 25 "
D.B.E. Conj. = 30 "
Exocy D.B (3) = 15 "
λ_{max} 284 "

9.



B.V = 253 nm
D.B.Ex. = 30 "
Ring Residue(8) = 40 "
λ_{max} 323 "

10.

253 nm B.value
20 " R. Residue
273 "

Note. If a conjugated polyene contains more than four double bonds, then Fieser-Kuhn rules are used. According to this approach, both λ_{max} and ε_{max} are related to the number of conjugated double bonds as well as other structural units by the following equations.

$$\lambda_{max} = 114 \times 5\ M + n\,(48.0 - 1.7n) - 16.5\ R_{endo} - 10\ R_{exo}$$

$$\in_{max} = (1.74 \times 10^{4})n$$

where

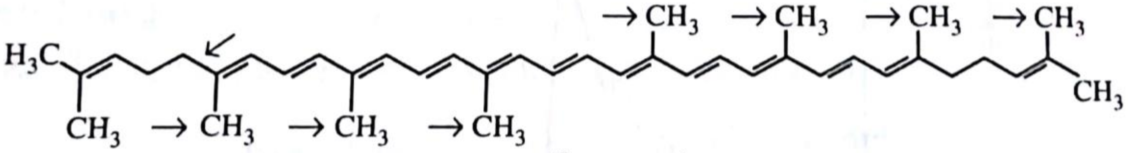
n = no. of conjugated double bonds.

M = no. of alkyl or alkyl like substituents on the conjugated system.

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system.

R_{exo} = no. of rings with exocyclic double bonds.

Consider the case of Lycopene :



(Lycopene)

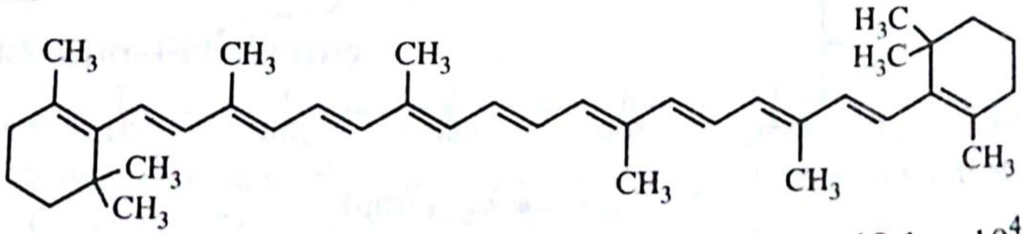
In this compound, only eleven double bonds are in conjugation. Thus, $n = 11$. In addition to this, there are eight substituents (methyl groups and chain residues). Thus, M = 8. As there is no ring system, there are neither exo nor endocyclic double bonds in this conjugated system. λ_{max} can be calculated as under :

$$\lambda_{max} = 114 + 5(8) + 11\ [48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm}$$

The observed value of λ_{max} is found to be 476 nm (hexane)

$$\varepsilon_{max} \text{ (calculated)} = 19.1 \times 10^{4}.$$

Similarly, λ_{max} can be calculated for β-carotene.



The calculated value of λ_{max} is found to be 453.3 nm and ε_{max} 19.1 × 10^{4}.

$$\lambda_{max}\,(\text{hexane}) = 114 + 5M + n(48{\cdot}0 - 1{\cdot}7n) - 16.5\,R_{endo} - 10R_{exo}$$

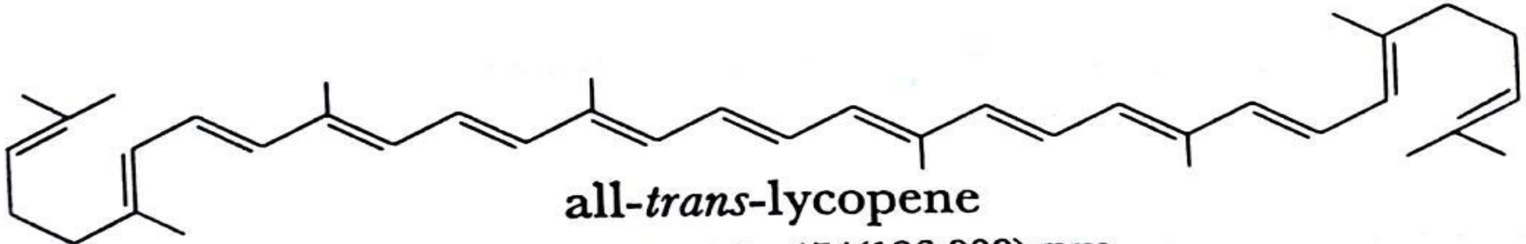
$$\epsilon_{max} = (1.74 \times 10^4)n \quad \text{where}$$

n = no. of conjugated double bonds

M = no. of alkyl or alkyl-like substituents on the conjugated system

R_{endo} = no. of rings with endocyclic double bonds in the conjugated system

R_{exo} = no. of rings with exocyclic double bonds



all-*trans*-lycopene

λ_{max}^{obs} 504(170,000); 474(186,000) nm

$$\lambda_{max}^{calc} = 114 + 5(8) + 11\,[48.0 - 1.7(11)] - 0 - 0 = 476 \text{ nm}$$

$$\lambda_{max}^{obs} = 474 \text{ nm (hexane)}$$

$$\epsilon_{max}^{cal.} = 1.74 \times 10^4(11) = 19.1 \times 10^4$$

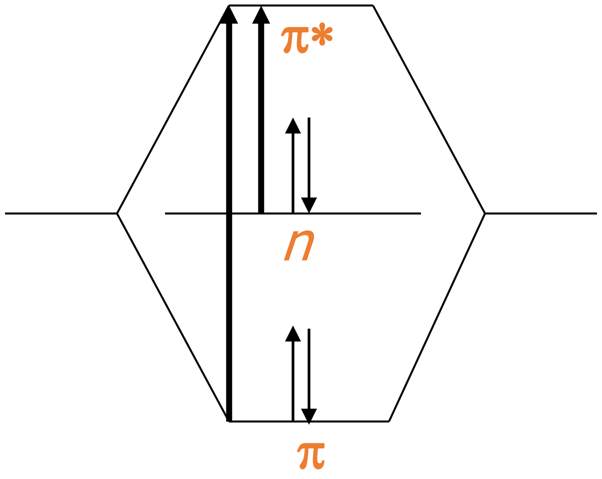
$$\epsilon_{max}^{obs}\,(\text{hexane}) = 18.6 \times 10^4$$

Structure Determination

B. Enones

1. General Features

Carbonyls, as we have discussed have two primary electronic transitions:



Remember, the π → π* transition is allowed and gives a high €, but lies outside the routine range of UV observation

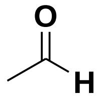
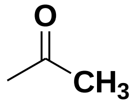
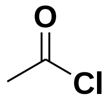
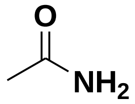
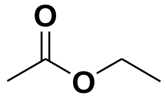
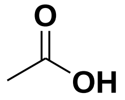
The *n* → π* transition is forbidden and gives a very low € , but can routinely be observed

IV. Structure Determination

B. Enones

1. General Features

For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the *n* → π* transition (λ_{max}):

	293 nm
	279
	235
	214
	204
	204

This is explained by the inductive withdrawal of electrons by O, N or halogen from the carbonyl carbon – this causes the *n*-electrons on the carbonyl oxygen to be held more firmly

It is important to note this is different from the auxochromic effect on π → π* which extends conjugation and causes a bathochromic shift

In most cases, this bathochromic shift is not enough to bring the π → π* transition into the observed range

IV. Structure Determination

B. Enones

1. General Features

Conversely, if the C=O system is conjugated both the *n* → π* and π → π* bands are bathochromically shifted

Here, several effects must be noted:

i. the effect is more pronounced for π → π*

ii. if the conjugated chain is long enough, the much higher intensity π → π* band will overlap and drown out the *n* → π* band

iii. the shift of the *n* → π* transition is not as predictable

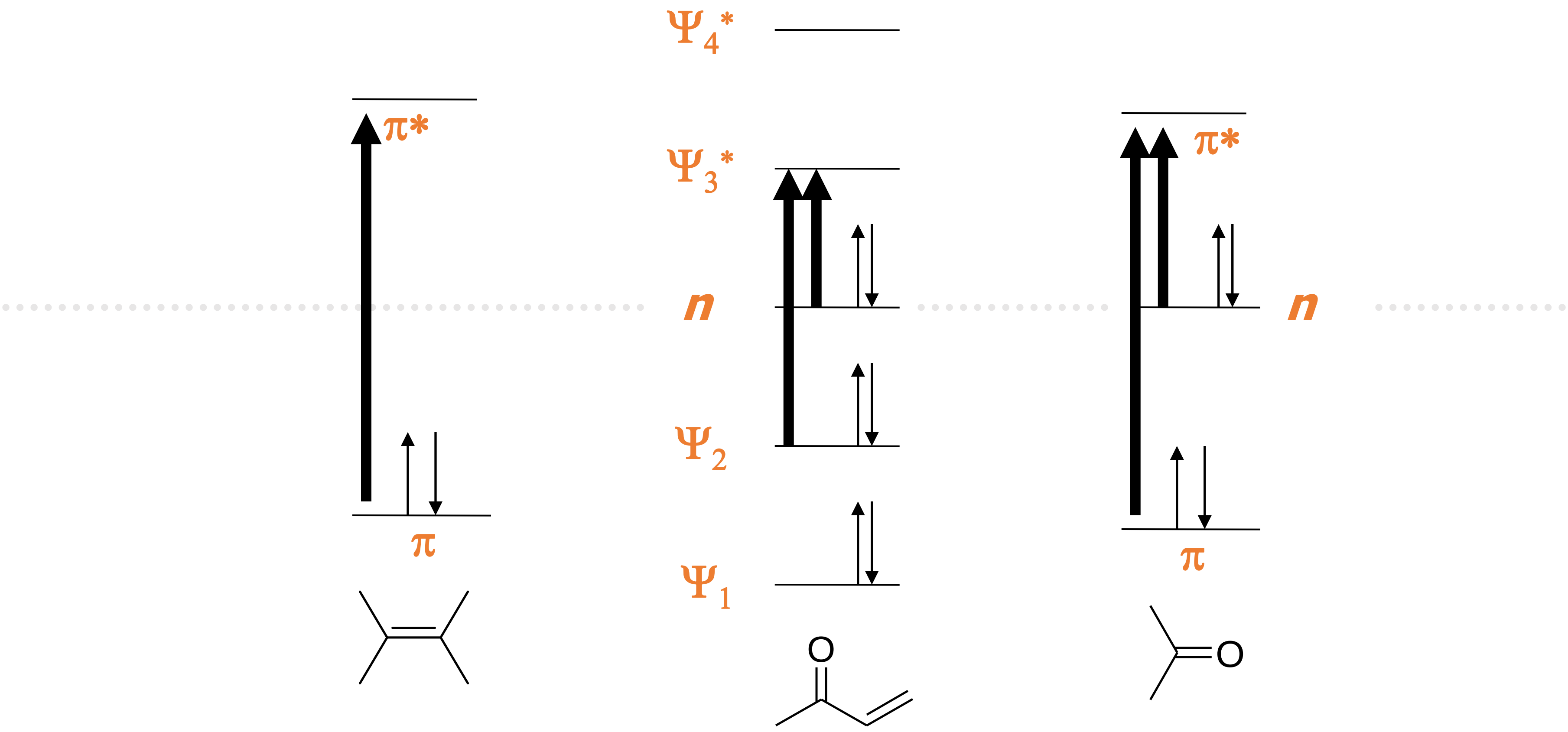
For these reasons, empirical Woodward-Fieser rules for conjugated enones are for the higher intensity, allowed π → π* transition

IV. Structure Determination

B. Enones

1. General Features

These effects are apparent from the MO diagram for a conjugated enone:



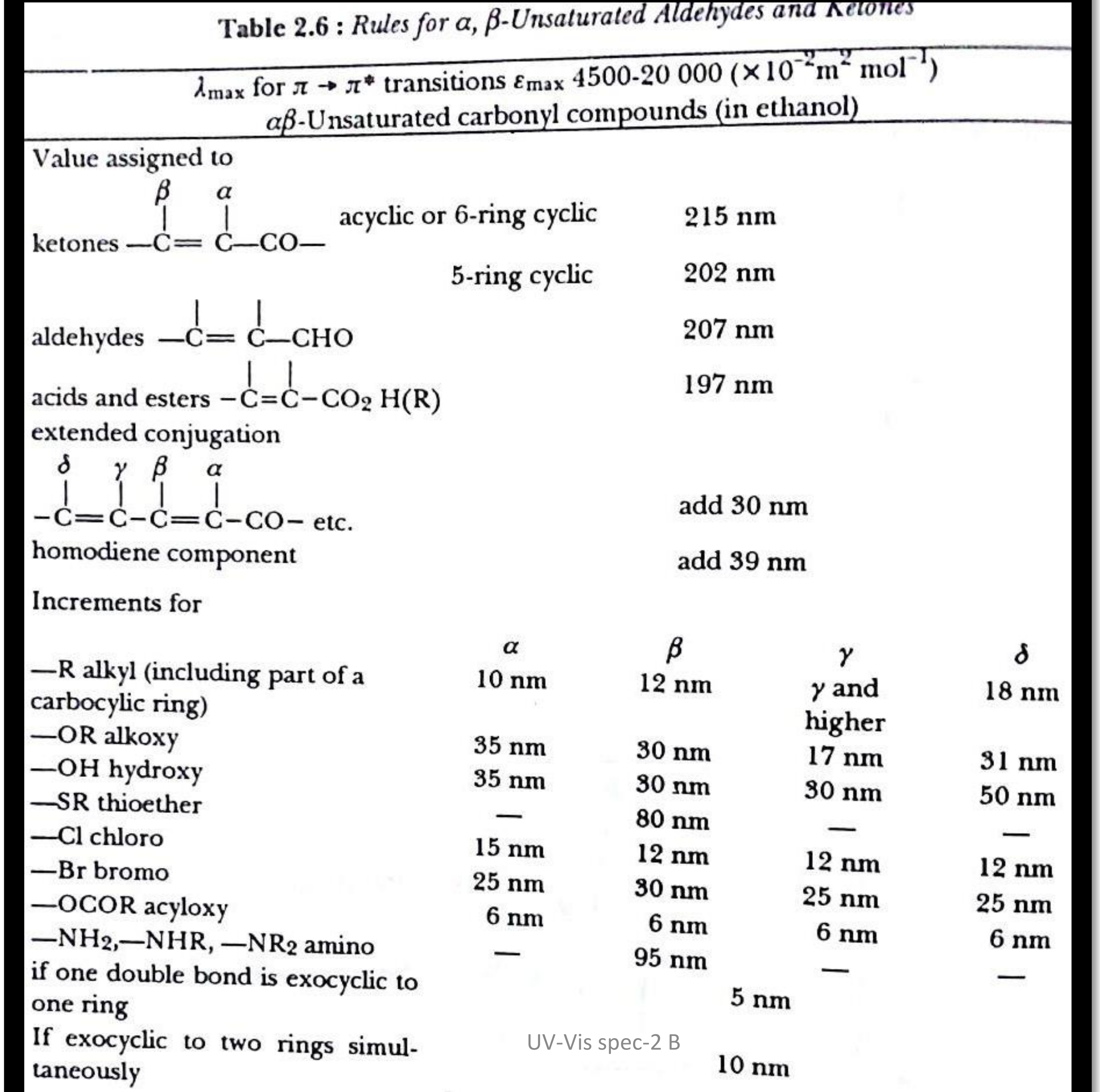


Table 2.6 : *Rules for α, β-Unsaturated Aldehydes and Ketones*

λ_{max} for $\pi \rightarrow \pi^*$ transitions ε_{max} 4500-20 000 ($\times 10^{-2} m^2 mol^{-1}$)
$\alpha\beta$-Unsaturated carbonyl compounds (in ethanol)

Value assigned to		
ketones $-\overset{\beta}{\underset{}{C}}=\overset{\alpha}{C}-CO-$	acyclic or 6-ring cyclic	215 nm
	5-ring cyclic	202 nm
aldehydes $-\overset{\vert}{C}=\overset{\vert}{C}-CHO$		207 nm
acids and esters $-\overset{\vert}{C}=\overset{\vert}{C}-CO_2H(R)$		197 nm
extended conjugation $-\overset{\delta}{C}=\overset{\gamma}{C}-\overset{\beta}{C}=\overset{\alpha}{C}-CO-$ etc.		add 30 nm
homodiene component		add 39 nm

Increments for

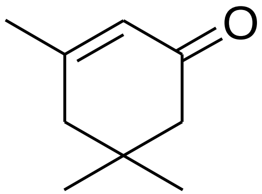
	α	β	γ	δ
—R alkyl (including part of a carbocylic ring)	10 nm	12 nm	γ and higher	18 nm
—OR alkoxy	35 nm	30 nm	17 nm	31 nm
—OH hydroxy	35 nm	30 nm	30 nm	50 nm
—SR thioether	—	80 nm	—	—
—Cl chloro	15 nm	12 nm	12 nm	12 nm
—Br bromo	25 nm	30 nm	25 nm	25 nm
—OCOR acyloxy	6 nm	6 nm	6 nm	6 nm
—NH_2,—NHR, —NR_2 amino	—	95 nm	—	—
if one double bond is exocyclic to one ring		5 nm		
If exocyclic to two rings simultaneously		10 nm		

Unlike conjugated alkenes, solvent does have an effect on λ_{max}

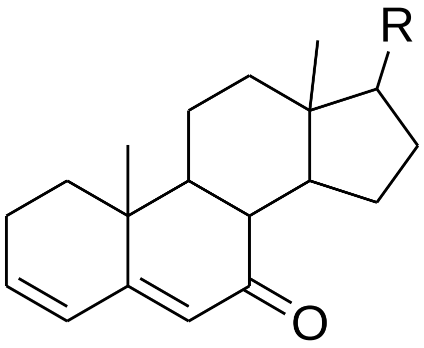
These effects are also described by the Woodward-Fieser rules

Solvent correction	Increment
Water	+8
Ethanol, methanol	0
Chloroform	-1
Dioxane	-5
Ether	-7
Hydrocarbon	-11

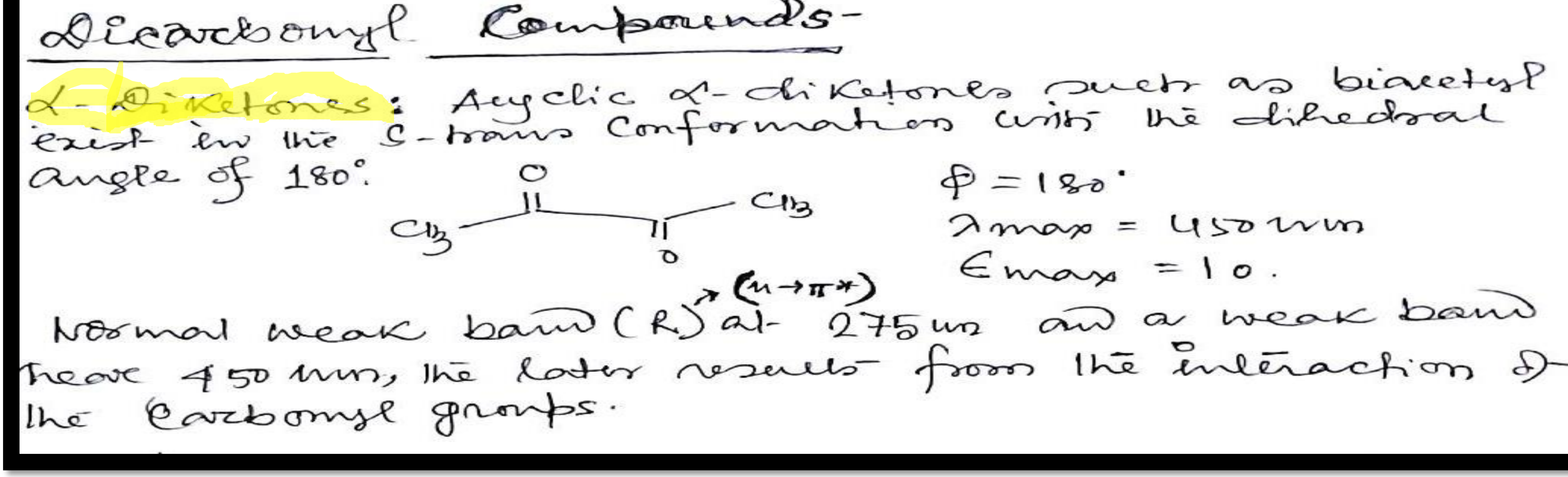
Some examples – keep in mind these are more complex than dienes



cyclic enone =		215 nm
2 x β- alkyl subs.	(2 x 12)	+24 nm
		239 nm
Experimental value		238 nm



cyclic enone =	215 nm
extended conj.	+30 nm
b-ring residue	+12 nm
d-ring residue	+18 nm
exocyclic double bond	+ 5 nm
	280 nm
Experimental	280 nm



Dicarbonyl Compounds-

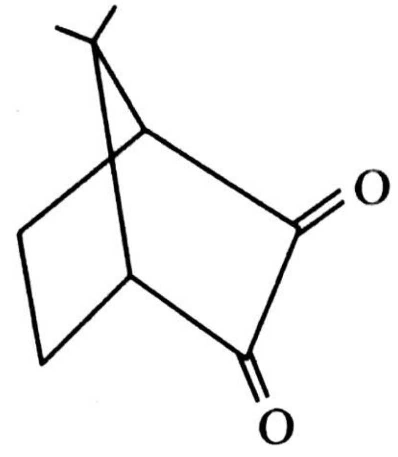
α-Diketones: Acyclic α-diketones such as biacetyl exist in the S-trans conformation with the dihedral angle of 180°.

$\phi = 180°$

$\lambda_{max} = 450\ nm$

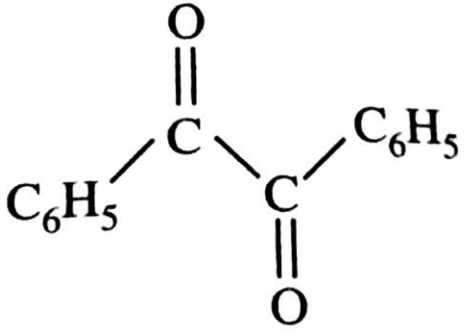
$\epsilon_{max} = 10$.

Normal weak band (R) $(n \rightarrow \pi^*)$ at 275 nm and a weak band near 450 nm, the later results from the interaction of the carbonyl groups.



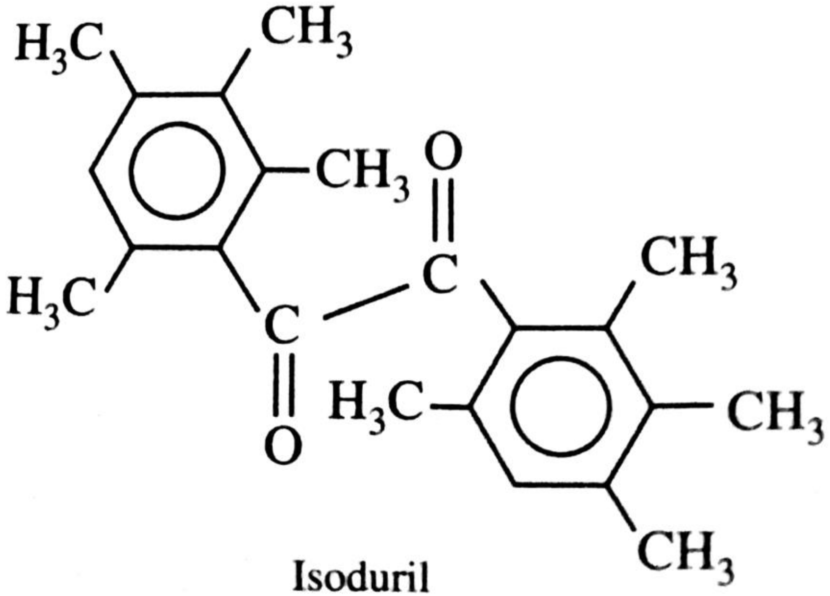
Camphoquinone
(I)
Dihedral angle 0-10°

$\lambda_{max} = 488$ nm
$\varepsilon_{max} = 17$



Benzil
(II)
Dihedral angle = 90°

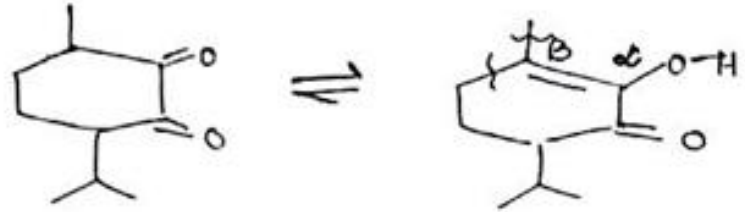
$\lambda_{max} = 370$ nm
$\varepsilon_{max} = 40$



Isoduril
(III)
Dihedral angle = 180°

The position of the long wave length band of α-diketones incapable of enolisation reflects the effect of coplanarity upon resonance, and hence depends upon dihedral angle, φ between the carbonyl groups

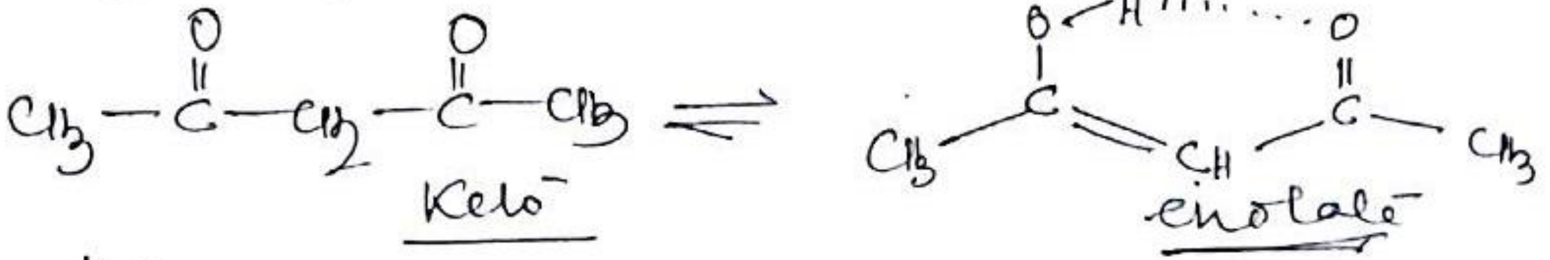
In cyclic dikones: The enolic forms are more stable, thus the absorption is related to that of an α, β unsaturated ~~system~~ carbonyl system. Six membered cyclic α-diketones largely exist in solution as enolic form. In strong alkaline solution λ max shifts to about 50 nm towards longer wave lengths, due to the formation of enolate ion.



Base value — 215 nm
2 β substituents — 24 "
α OH group — 35 "
λ_{max}^{EtOH} = 274 "

B – Diketones.

The UV spectra of B-diketones depend on degree of enolisation. The possibility of intra molecular hydrogen bonding stabilise the enolic form in acetyl acetone. The enolic species exists ~15% in aqueous solution. In vapour phase, or in solution of non polar solvents enolic form exists ~ 91-92%. The absorption is directly dependant on the concentration of the enol-form



$\lambda_{max}^{H_2O} = 274$ nm, $\epsilon_{max} = 2050$

$\lambda_{max}^{Isooctane} = 272$ nm, $\epsilon_{max} = 12000$

Thus intensity of absorptio increases drastically on changing solvent from pola to non polar.

cyclic β-diketones such as cyclohexane 1.3 dione exists almost exclusively in enolic form even in polar solvent. The enolic structures show strong absorption in 230-260 nm region due to π-π* transition in the S-trans enone system.

1,3 cyclohexanedione in ethanol absorbs at 253 nm (ϵ_{max} 22,000). The formation of enolate ion, in alkaline solution, shifts the strong absorption band into the 270-300 nm region.

enone

λmax calculation for enol form

Base value = 215

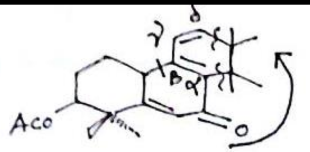
1 β subs = +12

β-OH = 30

λ^{EtOH}_{max} = 257 nm

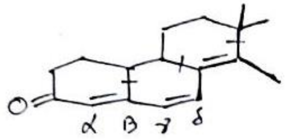
Observed value ≃ 253 nm

9.



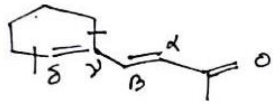
Base value	+ 215 nm
Homoannular diene	+ 39 nm
One double bond extended conjugation	+30
1 α ring residue	+10
1 β " "	+12
1 δ " "	+18
λ_{max}	324

10.



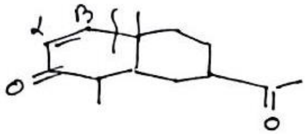
Base value	215 nm
2 double bond ext. Conj	60 "
2 exocyclic double bond	10 "
1 β- ring residue	12 "
1 (δ+1) " "	18
2 (δ+2) " "	36
λ_{max} =	351 nm

11.



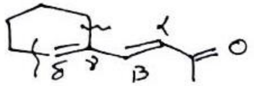
Base value	215 nm
Double bond ext	30
1 γ ring residue	18
1 δ " "	18
	281 "

12.



Base value	215 nm
1 β ring residue	12 "
	227 "

13.



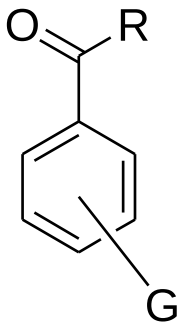
$215 + 30 + 18 + 18 = 281$

Aromatic System

Substituent Effects

d. Di-substituted and multiple group effects

Parent Chromophore	λ_{max}
R = alkyl or ring residue	246
R = H	250
R = OH or O-Alkyl	230



	Substituent increment		
G	*o*	*m*	*p*
Alkyl or ring residue	3	3	10
-O-Alkyl, -OH, -O-Ring	7	7	25
$-O^-$	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHC(O)CH_3$	20	20	45
$-NHCH_3$			73
$-N(CH_3)_2$	20	20	85

Aromatic system or Benzene Chromophore

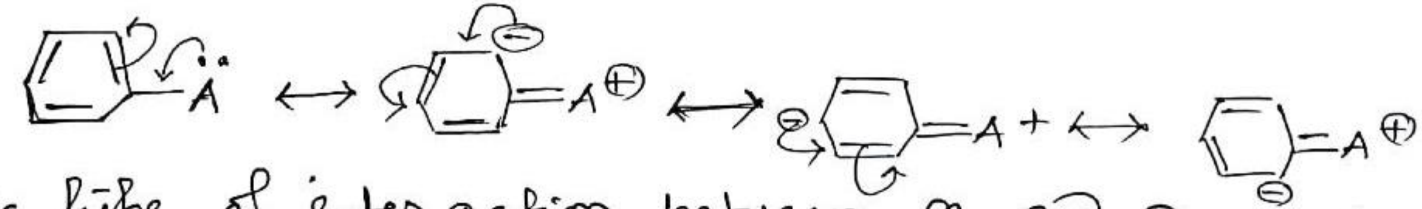
The electronic transition in benzene is mainly due to $\pi-\pi^*$ transition. In benzene three electronic transitions take place leading to three bands. Primary band at ~184 nm (ϵ_{max}: 48,000 ~~or 60,000?~~) and 202 nm (ϵ_{max} 7900) and a secondary band at 254 nm (ϵ_{max} : 200). The first one ie at 184 nm is the allowed transition

Effect of substituents on λ_{max} of Benzene :

Substituents in benzene ring can cause bathochromic and hyperchromic shifts.

A. Substituents with unshared electron pair. ⇒

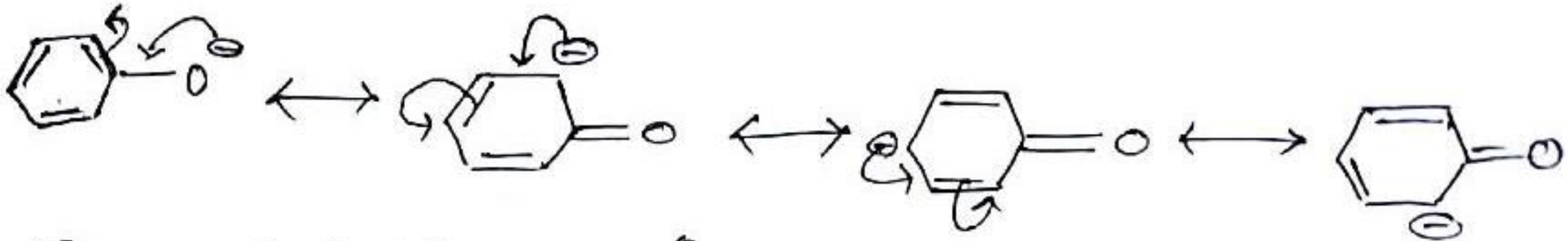
Substituents with unshared pair of electrons can shift the primary and secondary absorption bands. The non bonding electrons can increase the length of the π system through resonance.



This type of interaction between n and π electrons usually shifts the primary and secondary absorption bands of benzene to longer wave length.

On moving from benzene to phenol the primary band shifts by 7 nm towards longer wave length, while the secondary band by 16 nm.

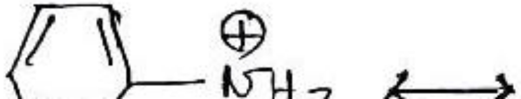
B **Phenol vs phenoxide ion:** Conversion of phenol to phenoxide ion results in bathochromic shift of the secondary band and the ϵ_{max} also increases, because the non bonding electron pair on oxygen becomes more available for delocalisation with π electron system of th than in phenol.



Aniline Vs Anilinium ion

On going from benzene to aniline the primary as well as the secondary band shift towards longer wave length ($204 \rightarrow 230$; $254 \rightarrow 280$ nm).

But when aniline is protonated these band shifts are not observed i.e it is found to behave almost same as benzene does. Because the lone pair of electrons on nitrogen becomes protonated and remaining no longer available for delocalisation with π electron system of benzene ring.

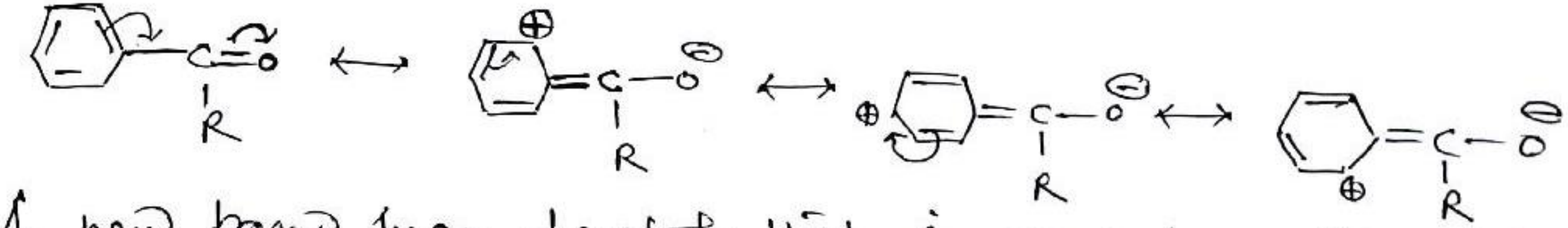


no further scope of delocalisation.

Alkyl substitution in benzene ring produces a bathochromic shift of secondary band (from 255 nm to 261 nm) with almost no report of primary band shift. This is due to the hyperconjugation of the σ electrons of alkyl C–H bond with π electron cloud of benzene ring.

The ortho di alkyl benzene absorbs at shorter wavelength (with lower ϵ_{max}) than that of the para isomer (with even higher ϵ_{max}). This can be explained on the basis of steric interaction in ortho substituents, which hinders the hyperconjugation.

π Conjugating substituents :



A new band may develop that is so intense that it may obscure (difficult to understand / view) the second band of benzene.

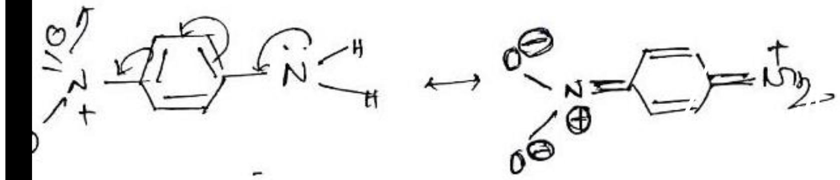
In this case the ring becomes electron deficient

Disubstituted Benzene.

Two cases may arise for para isomers.

Case - I — Both the groups are of same type (ie either both of them are electron releasing or both are electron withdrawing) the effect is same as that of mono substituted benzenes. The group having stronger effect controls the ~~shift~~ extent of shift.

Case-II If one is electron withdrawing, but the other is electron releasing, there is a pronounced red shift in the main absorption band. This is due to the extention of conjugation between the substituents through benzene ring.



But in case of ortho or meta, such extension is not possible.

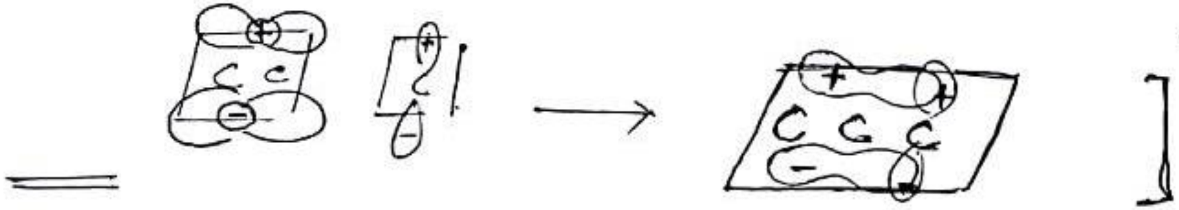
TRANS ANNULAR EFFECT

It is Clear that conjugation between $C=O$ and $C=C$ in ~~same~~ true sense results in bathochromic shift of the absorption bands of $C=O$ gr ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$)

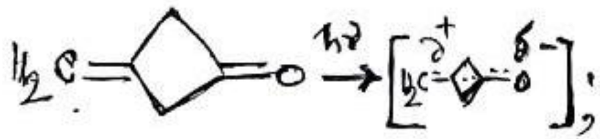
But some cases are found where these two groups are not conjugated to each other in CLASSICAL sense. These are generally cyclic systems, where the geometry / shape of the molecule enables them to involve in π overlap. This causes shift of the UV absorption band.

These type of interactions that apparently found to be non existant are known as TRANS ANNULAR conjugation.

Example : [The orbital overlap may occur in two ways. In π type overlap, the molecular orbitals (m.o) and atomic orbitals (a.o) overlap so as to retain the π bond nodal plane,



(iii)

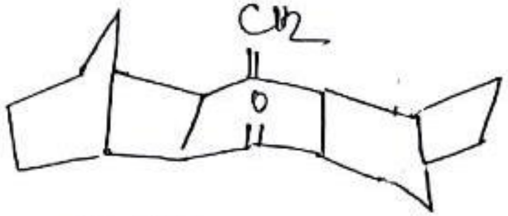


; π → π* 214 (moderately strong) n → π* 284 (weak)

3-Methylene cyclobutane

The UV-spectra closely matches with α, β unsaturated ketones.

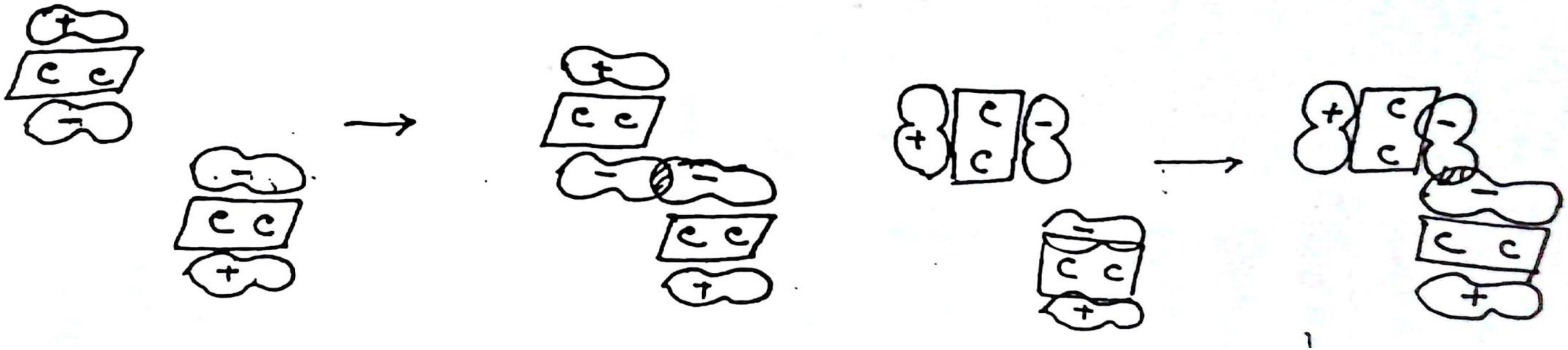
(ii)



π → π*
209.5

n → π*
298.4

there σ type overlap σ-π orbitals take


+
C C
−
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C C
+
+
C C
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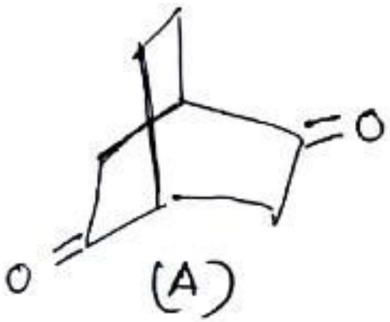
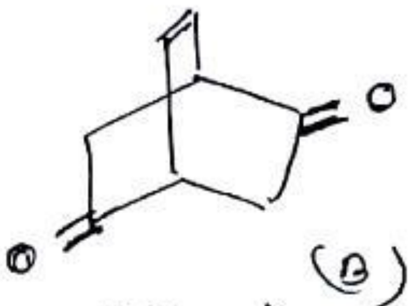
−
C C
+



(A)

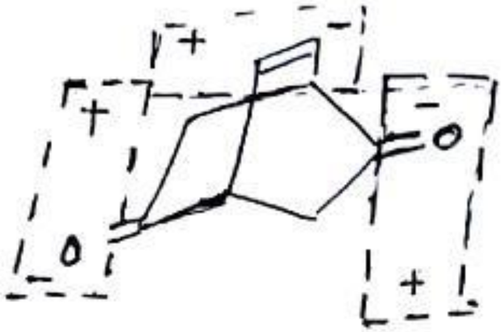
$n \rightarrow \pi^*$

$\lambda_{max} \rightarrow$ 296 nm.



(B)

≡

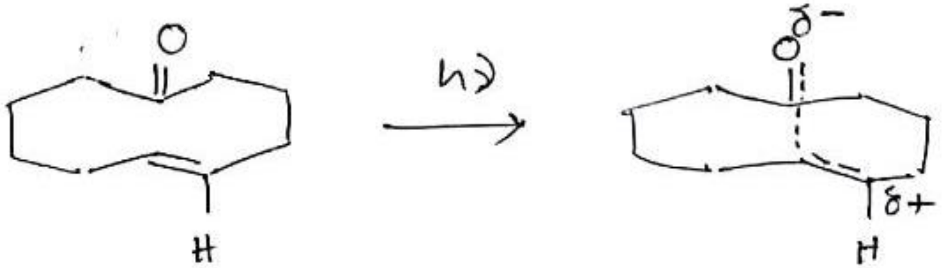


$\pi \rightarrow \pi^*$ 223 nm

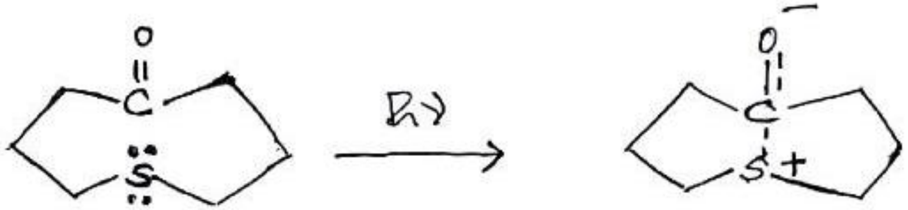
$n \rightarrow \pi^*$, 307; 296 nm

Compound (A) saturated bicyclic Ketone shows normal absorption of Carbonyl gr. But the unsaturated analogue (B) shows absorption pattern closely similar to α-β unsaturated Ketones. Here actually the C=C part takes part in σ type overlap of π orbitals of Carbonyl group.

It has been shown by Weinstein that while cyclodecanone and cis-cyclodeca-5-enone show a normal $n \rightarrow \pi^*$ absorption (289.9 nm), the trans analogue has an additional band. This third band is due to the weak bond ~~in~~ excited state, and the band so formed is known as PHOTO DESMOTIC BAND.



Similarly :-

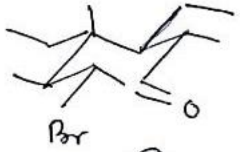


λ_{max} 238 nm

Here the π orbital of C=O group and the p (n) orbital of S overlaps.

Ⓐ

λ_{max} = 283 nm



Ⓑ

λ_{max} = 279 nm

Ⓒ

λ_{max} = 309 nm

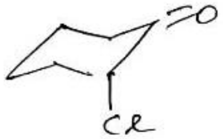
Introduction of α-Bromine atom eq ~~axial~~ Ⓑ lowers the n→π* transition by ~4–10 nm and increases by 10–30 nm when it is added axially ~~equatorially~~ Ⓒ in comparison with the parent compound Ⓐ.

(D)

λ_{max} 282 nm

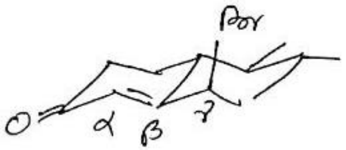
(E)

λ_{max} 2 - nm



(F)

λ_{max} ~ 293 nm



Here also the axial substituent causes shift of n→π* towards longer wavelength and equatorial to shorter (comparison with unsubstituted one).

UV Spectroscopy

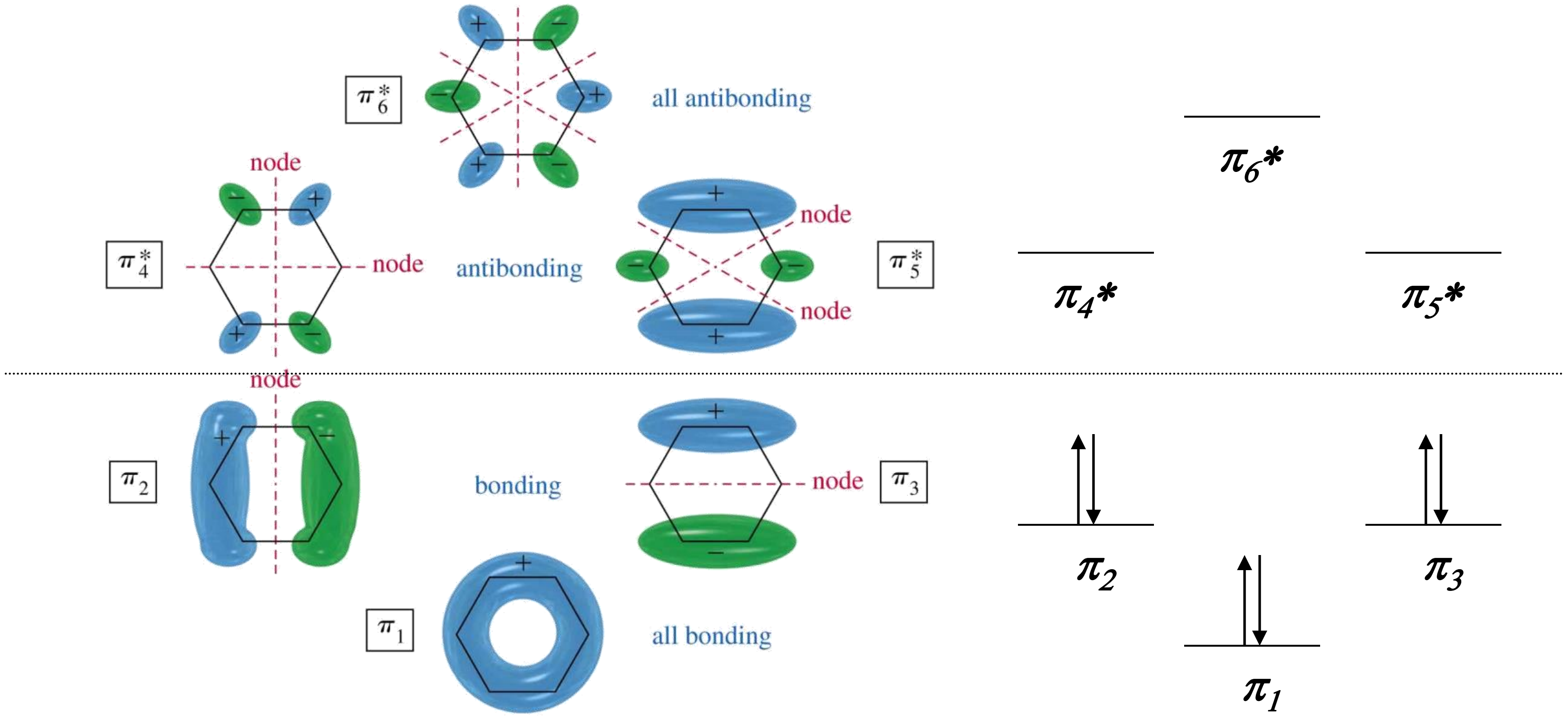
Structure Determination

C. Aromatic Compounds

1. General Features

Although aromatic rings are among the most widely studied and observed chromophores, the absorptions that arise from the various electronic transitions are complex

On first inspection, benzene has six π-MOs, 3 filled π, 3 unfilled π^*



UV Spectroscopy

Visible Spectroscopy

- A. Color
  - 1. General
    - The portion of the EM spectrum from 400-800 is observable to humans- we (and some other mammals) have the adaptation of seeing color at the expense of greater detail

	λ, nm
Violet	400-420
Indigo	420-440
Blue	440-490
Green	490-570
Yellow	570-585
Orange	585-620
Red	620-780

UV Spectroscopy

Visible Spectroscopy

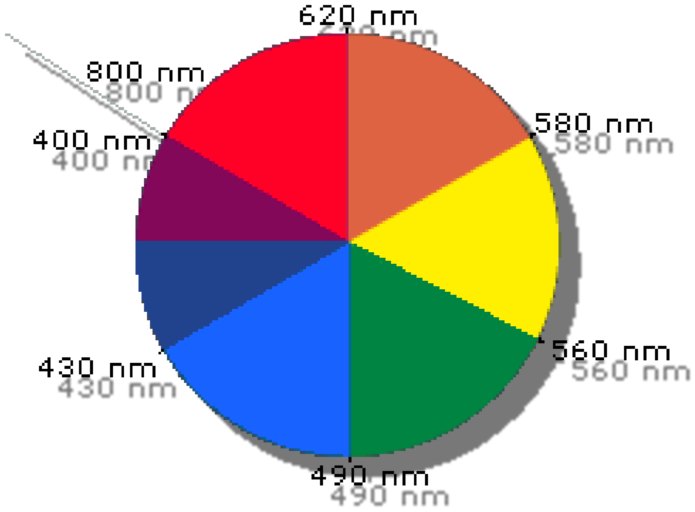
A. Color

1. General

- When white (continuum of λ) light passes through, or is reflected by a surface, those ls that are absorbed are removed from the transmitted or reflected light respectively

- What is "seen" is the complimentary colors (those that are not absorbed)

- This is the origin of the "color wheel"



UV Spectroscopy

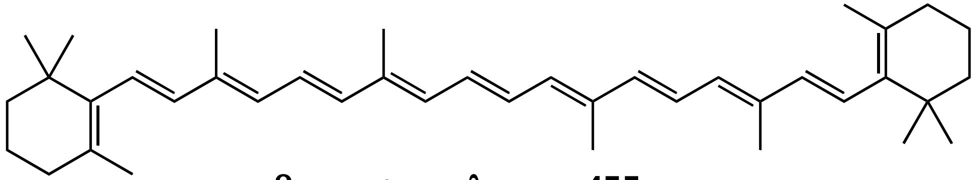
V. Visible Spectroscopy

A. Color

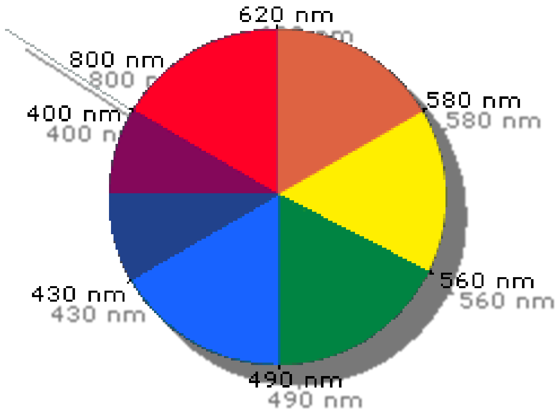
1. General

- Organic compounds that are “colored” are typically those with extensively conjugated systems (typically more than five)

- Consider β-carotene



β-carotene, λ_{max} = 455 nm

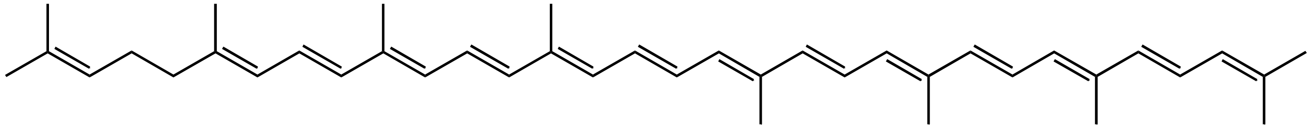


λ_{max} is at 455 – in the far blue region of the spectrum – this is absorbed

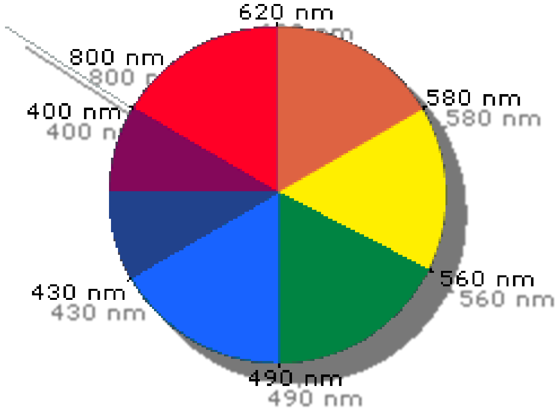
The remaining light has the complementary color of orange

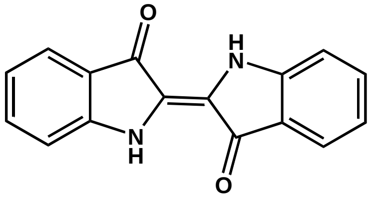
UV Spectroscopy

V. Visible Spectroscopy
    A. Color
        1. General
            - Likewise:



lycopene, λ_{max} = 474 nm





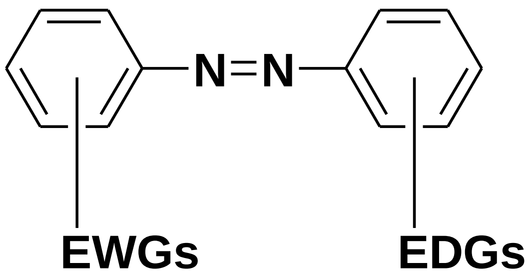
indigo

λ_{max} for lycopene is at 474 – in the near blue region of the spectrum – this is absorbed, the compliment is now red

λ_{max} for indigo is at 602 – in the orange region of the spectrum – this is absorbed, the compliment is now indigo!

UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - One of the most common class of colored organic molecules are the azo dyes:

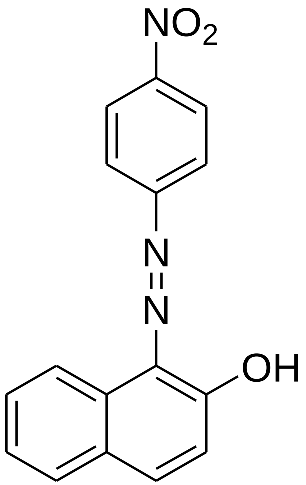


From our discussion of di-subsituted aromatic chromophores, the effect of opposite groups is greater than the sum of the individual effects – more so on this heavily conjugated system

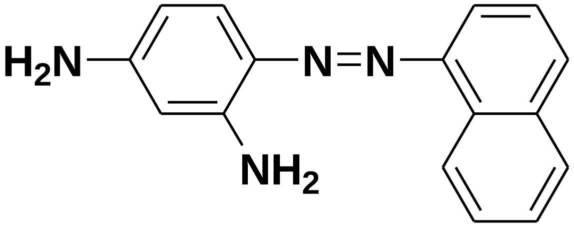
Coincidentally, it is necessary for these to be opposite for the original synthetic preparation!

UV Spectroscopy

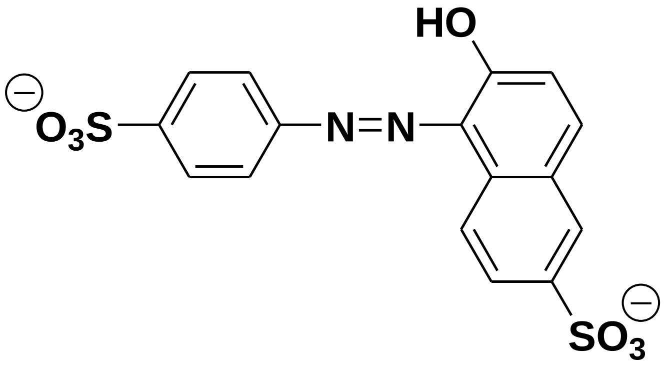
V. Visible Spectroscopy
  A. Color
    1. General
      - These materials are some of the more familiar colors of our "environment"



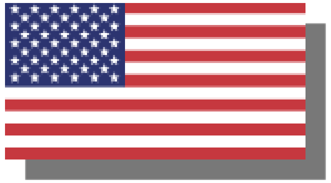
Para Red

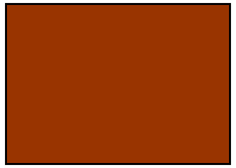


Fast Brown



Sunset Yellow (Food Yellow 3)



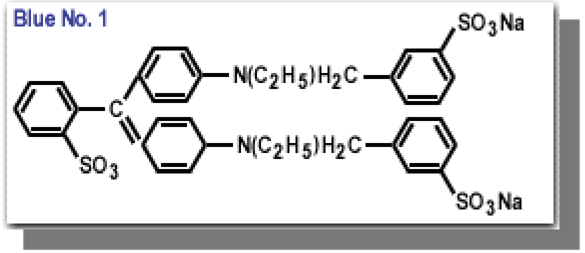


The colors of M&M’s

Bright Blue

Common Food Uses

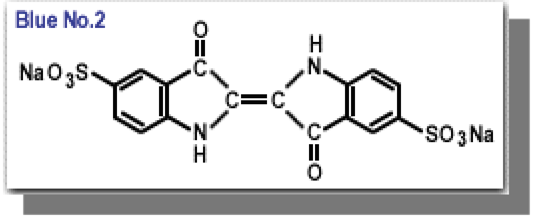
Beverages, dairy products, powders, jellies, confections, condiments, icing.


Blue No. 1

Royal Blue

Common Food Uses

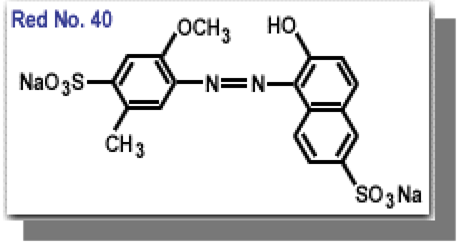
Baked goods, cereals, snack foods, ice-cream, confections, cherries.


Blue No.2

Orange-red

Common Food Uses

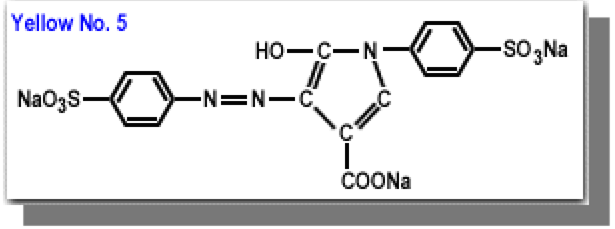
Gelatins, puddings, dairy products, confections, beverages, condiments.


Red No. 40

Lemon-yellow

Common Food Uses

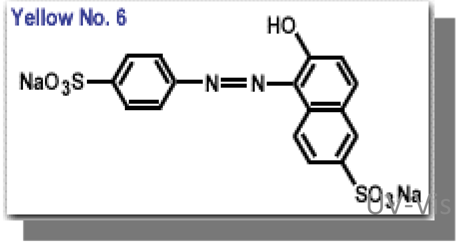
Custards, beverages, ice-cream, confections, preserves, cereals.


Yellow No. 5

Orange

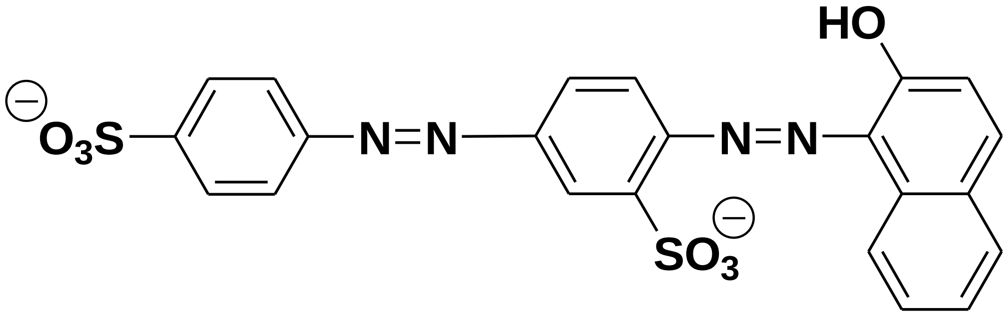
Common Food Uses

Cereals, baked goods, snack foods, ice-cream, beverages, dessert powders, confections


Yellow No. 6

UV Spectroscopy

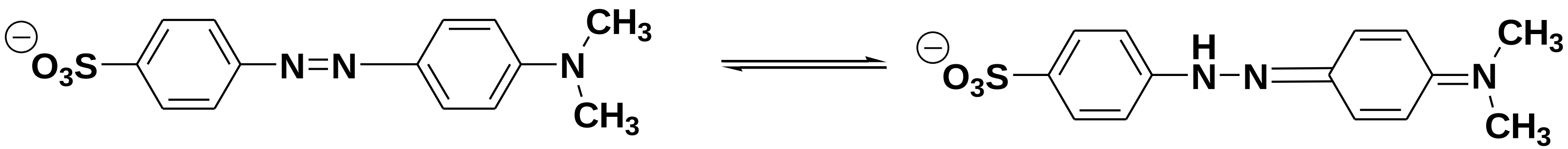
V. Visible Spectroscopy
  A. Color
    1. General
      - In the biological sciences these compounds are used as dyes to selectively stain different tissues or cell structures
      - Biebrich Scarlet - Used with picric acid/aniline blue for staining collagen, recticulum, muscle, and plasma. Luna's method for erythrocytes & eosinophil granules. Guard's method for sex chromatin and nuclear chromatin.



UV Spectroscopy

V. Visible Spectroscopy
  A. Color
    1. General
      - In the chemical sciences these are the acid-base indicators used for the various pH ranges:
      - Remember the effects of pH on aromatic substituents

Methyl Orange



Yellow, pH > 4.4

Red, pH < 3.2