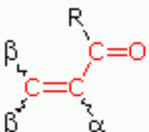
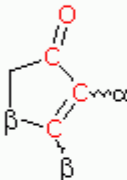
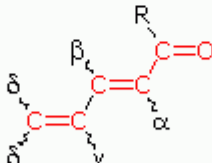
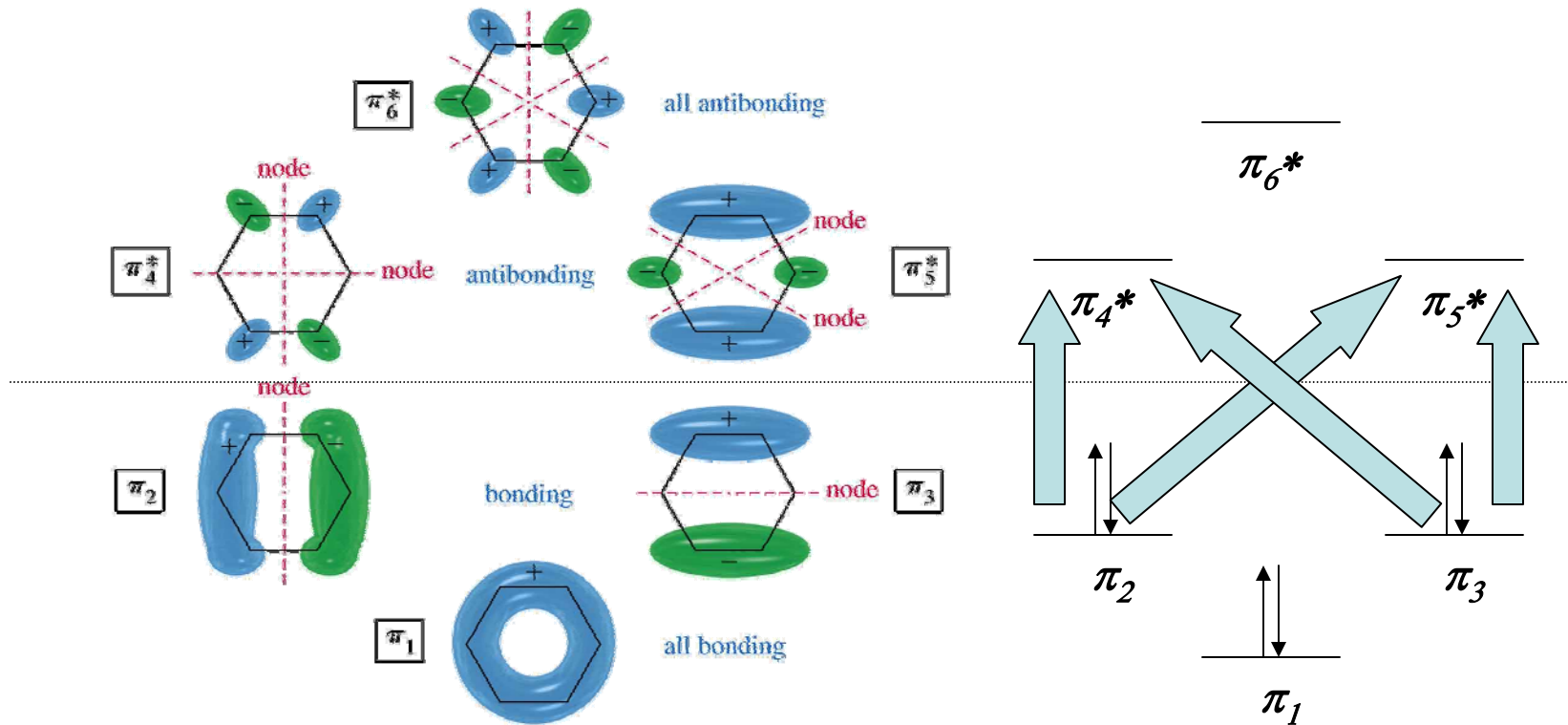


Woodward-Fieser Rules for Calculating the $\pi \rightarrow \pi^*$ λ_{\max} of Conjugated Carbonyl Compounds

Core Chromophore	Substituent and Influence
 <p>R = Alkyl 215 nm R = H 210 nm R = OR' 195 nm</p>	<p>α- Substituent</p> <p>R- (Alkyl Group) +10 nm Cl- (Chloro Group) +15 Br- (Chloro Group) +25 HO- (Hydroxyl Group) +35 RO- (Alkoxy Group) +35 RCO₂- (Acyl Group) +6</p>
 <p>Cyclopentenone 202 nm</p>	<p>β- Substituent</p> <p>R- (Alkyl Group) +12 nm Cl- (Chloro Group) +12 Br- (Chloro Group) +30 HO- (Hydroxyl Group) +30 RO- (Alkoxy Group) +30 RCO₂- (Acyl Group) +6 RS- (Sulfide Group) +85 R₂N- (Amino Group) +95</p>
	<p>γ & δ- Substituents</p> <p>R- (Alkyl Group) +18 nm (both γ & δ) HO- (Hydroxyl Group) +50 nm (γ) RO- (Alkoxy Group) +30 nm (γ)</p> <p align="center">Further π-Conjugation</p> <p>C=C (Double Bond) ... +30 C₆H₅ (Phenyl Group) ... +60</p>
<p>(i) Each exocyclic double bond adds 5 nm. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.</p> <p>(ii) Homoannular cyclohexadiene component adds +35 nm (ring atoms must be counted separately as substituents)</p> <p>(iii) <u>Solvent Correction</u>: water = -8; methanol/ethanol = 0; ether = +7; hexane/cyclohexane = +11</p>	

$$\lambda_{\max} (\text{calculated}) = \text{Base} + \text{Substituent Contributions and Corrections}$$

Substituted Benzenes



Symmetry and selection rules limit actual transitions:

~185 nm ($\epsilon \sim 60,000$), “primary band” or “E band”

~204 nm ($\epsilon \sim 8,000$), “second primary band” or “K band”

~256 nm ($\epsilon \sim 200$), “secondary band” or “B band”

Substituted Benzenes

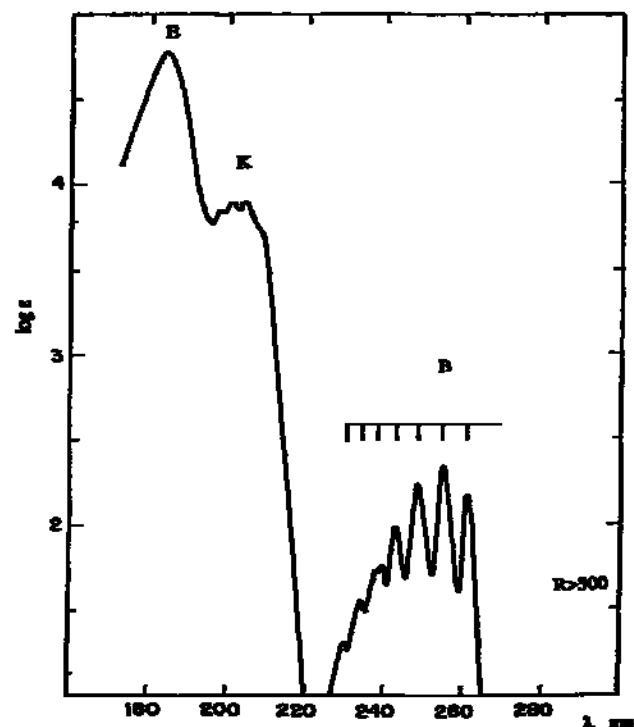
8.4.2

UV Absorption of Substituted Benzenes

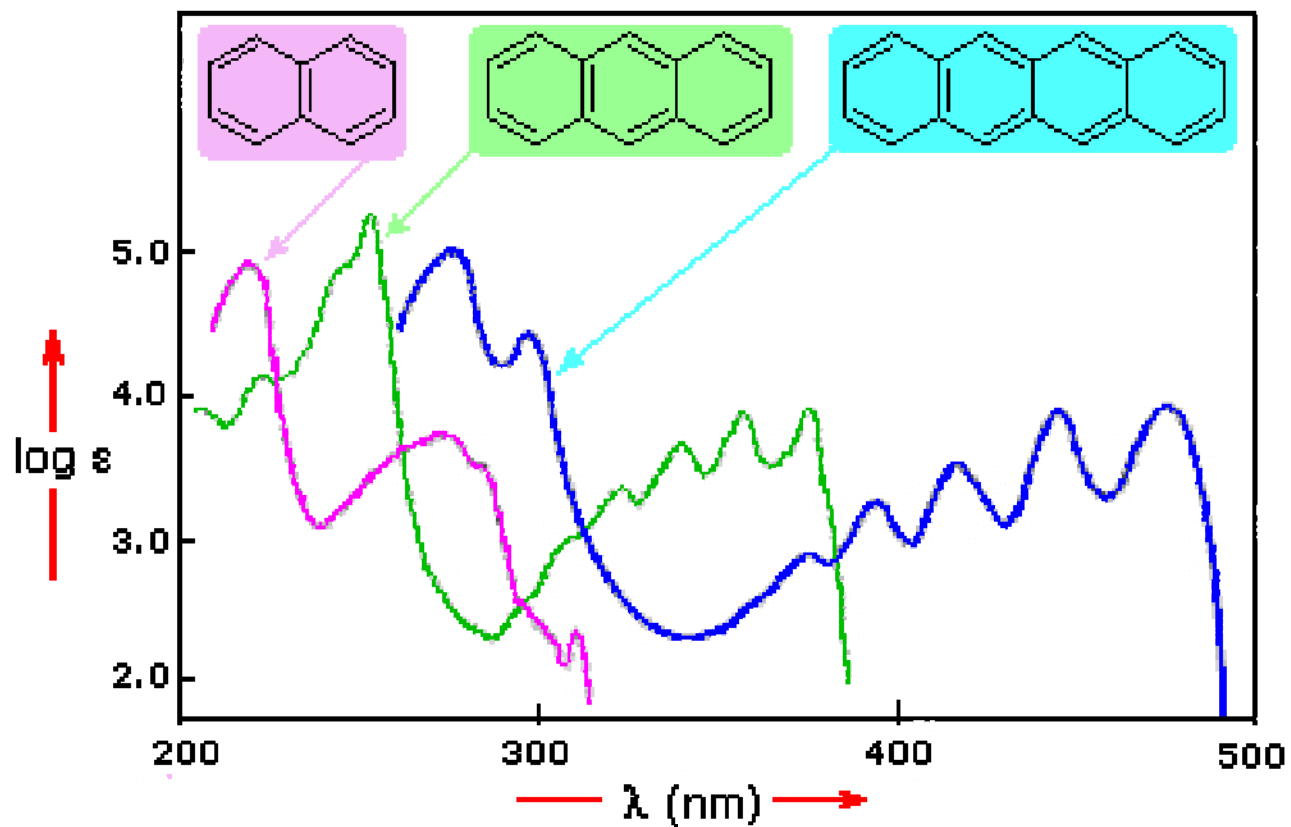
Estimation of the position of the allowed π - π^* transition in multiply substituted benzenes (λ_{max} in nm, $\log \epsilon: \approx 4$)

Base value: 203.5

Substituent	Increment [nm]
-CH ₃	3.0
-Cl	6.0
-Br	6.5
-OH	7.0
-O ⁻	31.5
-OCH ₃	13.5
-NH ₂	26.5
-NHCOCH ₃	38.5
-NO ₂	65.0
-CN	20.5
-CHO	46.0
-COCH ₃	42.0
-COOH	25.5



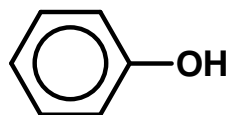
Polyaromatics



Substituent Effects on Aromatic Absorption

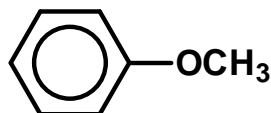
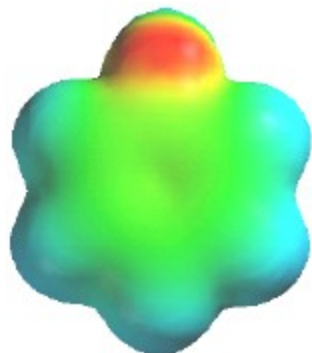
256 nm band is sensitive to electron density of aromatic ring

ϵ units = $L \text{ mole}^{-1} \text{ cm}^{-1}$



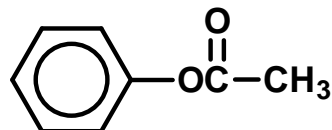
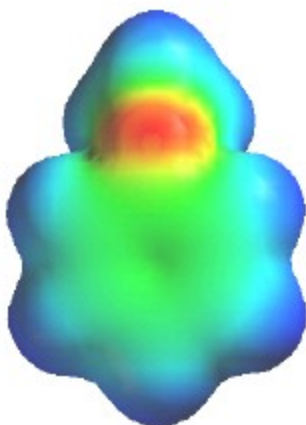
270 nm (ϵ 1,450)

PHENOL



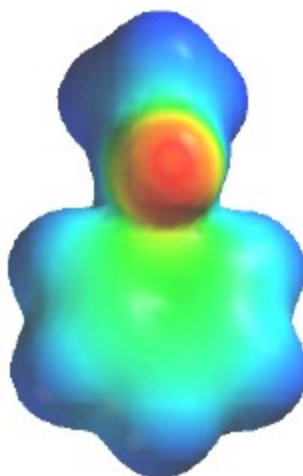
287 nm (ϵ 2,600)

ANISOLE



258 nm (ϵ 250)

PHENYL ACETATE



The Influence of Various Directing Groups and Atoms

Ortho-Para Directors	Meta Directors
Strong	Strong
<ul style="list-style-type: none"> —NH₂ —NHR —NR₂ —OH —O⁻ 	<ul style="list-style-type: none"> —NO₂ —NH₃⁺ —NR₃⁺ —CF₃ —CCl₃
Moderate	Moderate
<ul style="list-style-type: none"> —NHCOCH₃ —NHCOR —OCH₃ —OR —CHO —COR 	<ul style="list-style-type: none"> —C\equivN —SO₃H —COOH —COOR
Weak	Weak
<ul style="list-style-type: none"> —CH₃ —CH₂CH₃ —R —C₆H₅ 	

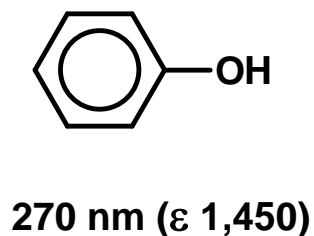
Electron density

Red = highest

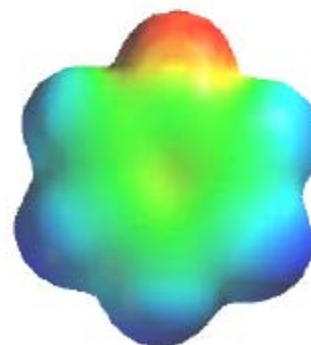
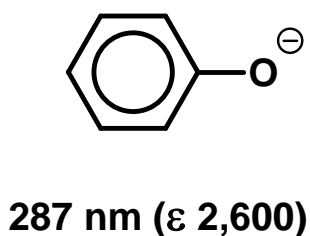
Green = moderate

pH Effects on Aromatic Absorption

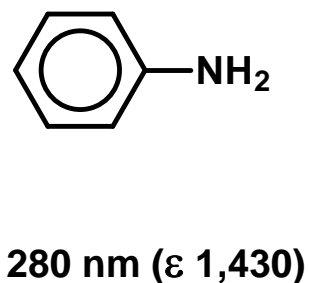
ϵ units = L mole⁻¹ cm⁻¹



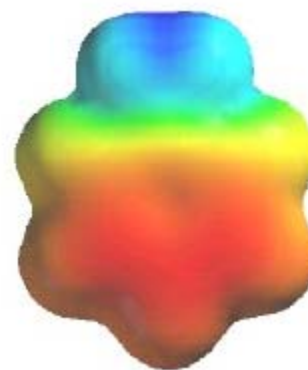
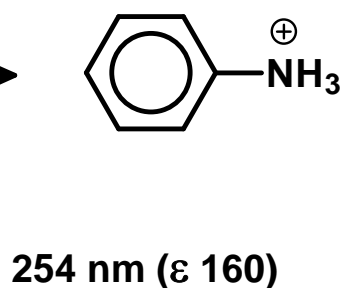
base \rightarrow



Phenoxide ion
electrostatic
potential map



\rightarrow



Anilinium ion
electrostatic
potential map

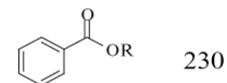
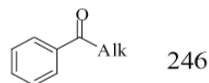
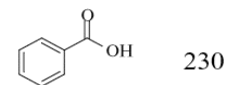
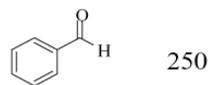
Aromatic Carbonyl Compounds

8.4.3

UV Absorption of Aromatic Carbonyl Compounds

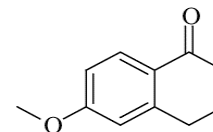
Scott rules for estimating the position of the K band
(solvent: ethanol; λ_{max} in nm, ϵ : 10000–30000)

Parent system:



Increments	Substituent	<i>ortho</i>	<i>meta</i>	<i>para</i>
	–alkyl	3	3	10
	–cycloalkyl	3	3	10
	–Cl	0	0	10
	–Br	2	2	15
	–OH	7	7	25
	–O–alkyl	7	7	25
	–O [–]	11	20	78
	–NH ₂	13	13	58
	–N(CH ₃) ₂	20	20	85
	–NHCOCH ₃	20	20	45

Example: Estimation of the absorption maximum (K band) for



base value	246
<i>ortho</i> -cycloalkyl	3
<i>para</i> -O-alkyl	25
estimated	274
exp	276

Pretsch/Buhlmann/Affolter/Badertscher,
*Structure Determination of Organic
Compounds*

Woodward Rules for Enones

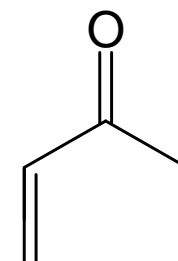
- Base values

- acyclic or 6-membered ring

215 nm

- 5-membered ring

202 nm



- Additions for

- double bond extending conjugation 30 nm

- alkyl group or ring residue

α 10 nm

β 12 nm

\downarrow γ 18 nm

- hydroxyl group

α 35 nm

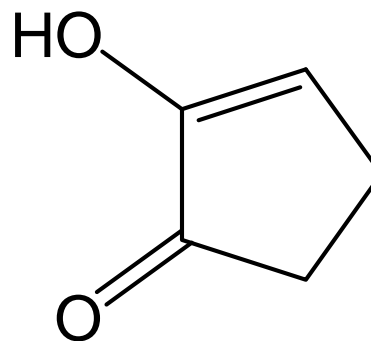
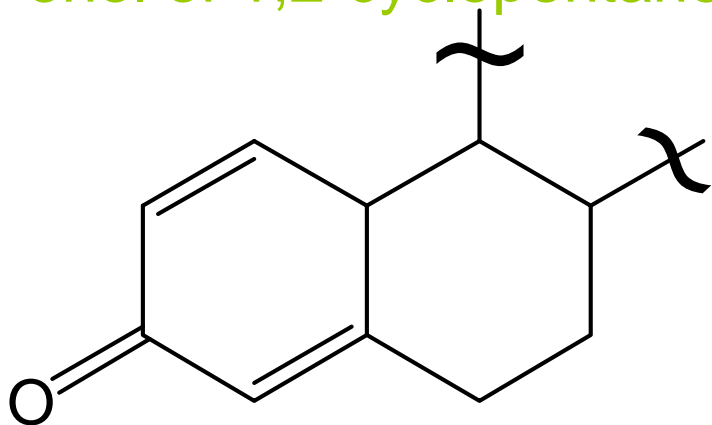
β 30 nm

exocyclic double bond

5 nm

Are you getting the concept?

Predict the absorption λ_{max} for cholesta-1,4-dien-3-one and the enol of 1,2-cyclopentanedione.



Common Solvents

8.6 UV/Vis Absorption of Common Solvents

The end absorption, λ_{end} , of several common solvents is given here as the wavelength at which the solvents absorb 80% of the irradiated light (λ_{end} in nm; cell length, 1 cm; reference, water).

Solvent	λ_{end}	Solvent	λ_{end}
acetone	335	ethyl acetate	205
acetonitrile	190	heptane	195
benzene	285	hexane	195
carbon disulfide	380	methanol	205
carbon tetrachloride	265	pentane	200
chloroform	245	2-propanol	205
cyclohexane	210	pyridine	305
dichloromethane	230	tetrahydrofuran	230
diethyl ether	210	toluene	285
1,4-dioxane	215	2,2,4-trimethylpentane	210
ethanol	205	xylene	290