تفريغ تحليل آلي

اسم الموضوع: الشابتر ٢٤ الجزء

إعداد الصيدلاني/ـة: لمى منصور

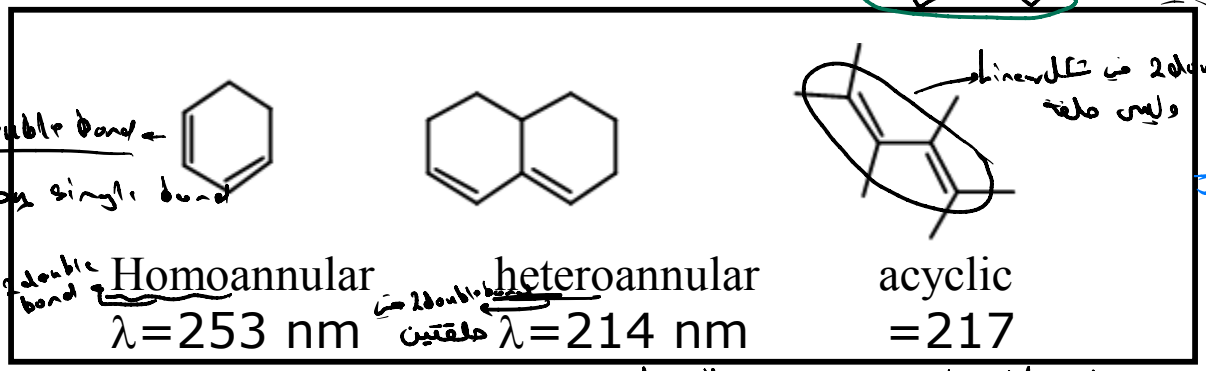
Seul Academy

لجان التوعية

Empirical Rules for Calculating Uv/Vis Absorptions

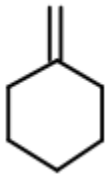
Woodward-Fieser Rules for Calculating the λmax of Conjugated Dienes and Polyenes

- Parent:



- Increments for:

Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5



exocyclic

Polar groupings:

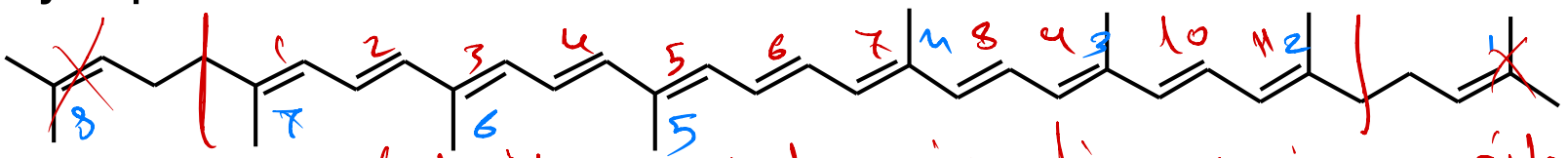
-OC(O)CH3	+0
-OR	+6
-Cl, -Br	+5
-NR2	+60
-SR	+30

For more than 4 conjugated double bonds:

λ_{max} = 114 + 5(number of alkyl groups) + n(48.0-1.7n)

Example:

Lycopene:



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

λ_{max}(Actual) = 474.

١- اول خطوة من خطوات الحل لتحديد acyclic . parent

2- ثاني خطوة الشوف اذا احنا امتداد لـ conjugation ✗

3- اذا احنا 3 alkyl substituent

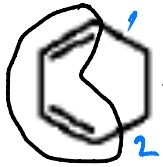
Example 1:

→ acyclic

Transoid:		217 nm
Alkyl groups or ring residues:	3 x 5 =	15 nm
Calculated:		232 nm
Observed:		234 nm

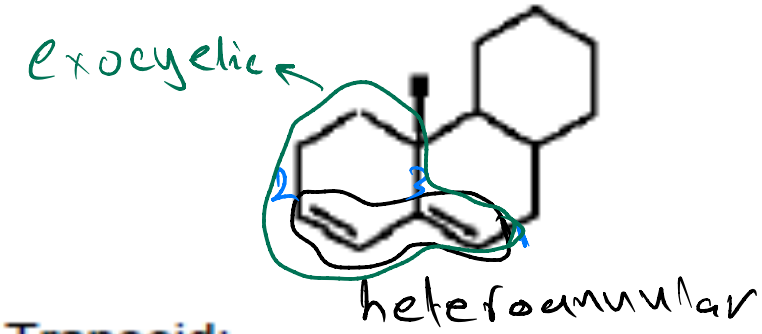
← تكون calculated اقل من observed

Example 2:

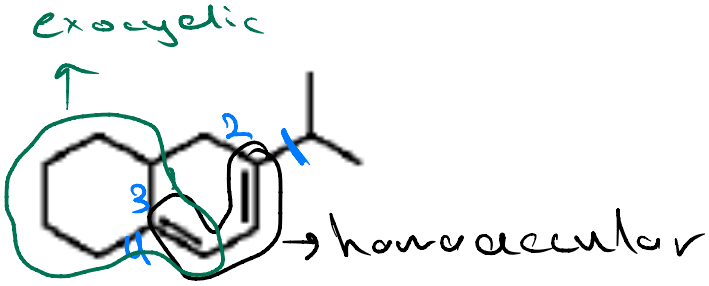


→ homo annular

Cisoid:		253 nm
Alkyl groups or ring residues:	2 x 5 =	10 nm
Calculated:		263 nm
Observed:		256 nm



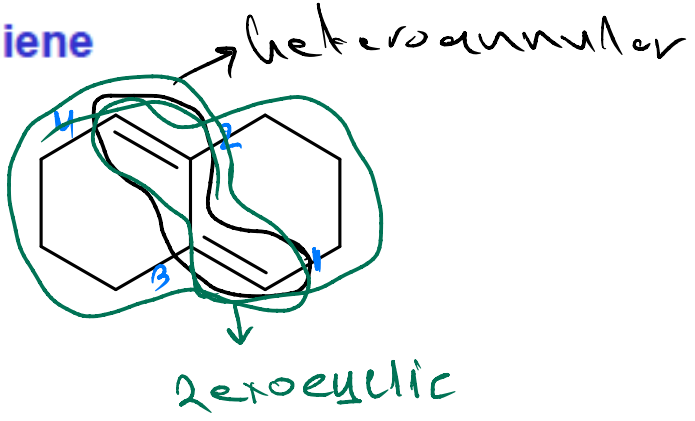
Transoid:		214 nm
Alkyl groups or ring residues:	3 x 5 =	15 nm
Exocyclic double bond:		5 nm
Calculated:		234 nm
Observed:		235 nm



Cisoid:		253 nm
Alkyl groups or ring residues:	4 x 5 =	20 nm
Exocyclic double bond:		5 nm
Calculated:		278 nm
Observed:		275 nm

Example 1

Calculate the λ_{max} for 1,4, dibenzodiene



Solution:

The structure is

Parent heterodiene = 214

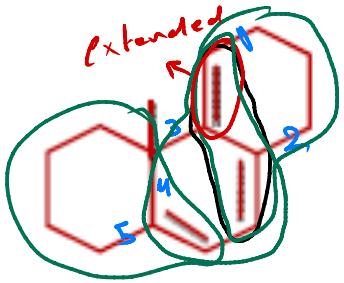
Alkyl substituents (4x5 nm) = 20

Exocyclic double bond 2x5 = 10

λ_{max} = 244 nm (observed 247 nm)

Example 2

Calculate the λ_{max} for



Solution:

The compound is a homoannular diene

Base value	= 253
Ring residues (5x5)	= 25
Exocyclic double bond 3x5	= 15
Extended C=C	= 30

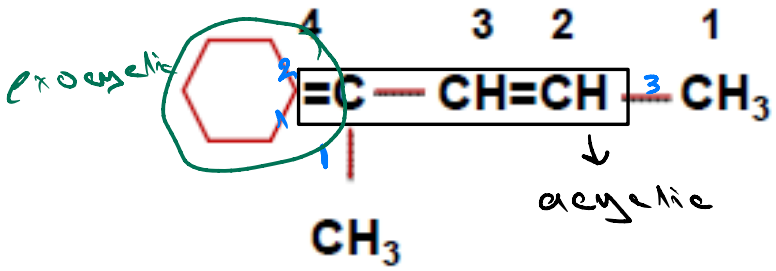
λ_{max} is 323 nm

observed value is 320 nm.

Example 3

Calculate the absorption maximum for 4 cyclohexenyl 2-pentene

Solution



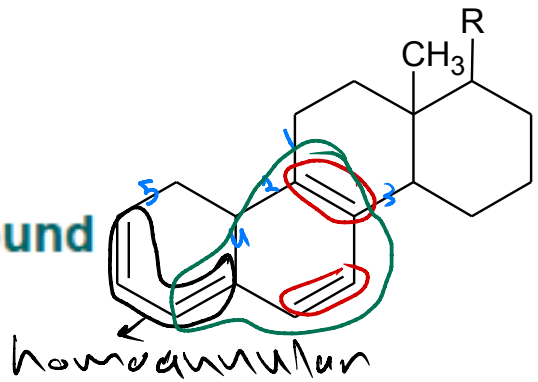
It is a 2, 4 diene system

Base value	**217**
2 Alkyl substituents 2x5	**10**
2 Ring residues 2x5	**10**
1 Exocyclic bond	**5**
	242 nm

Observed value is also 242 nm

Example 4

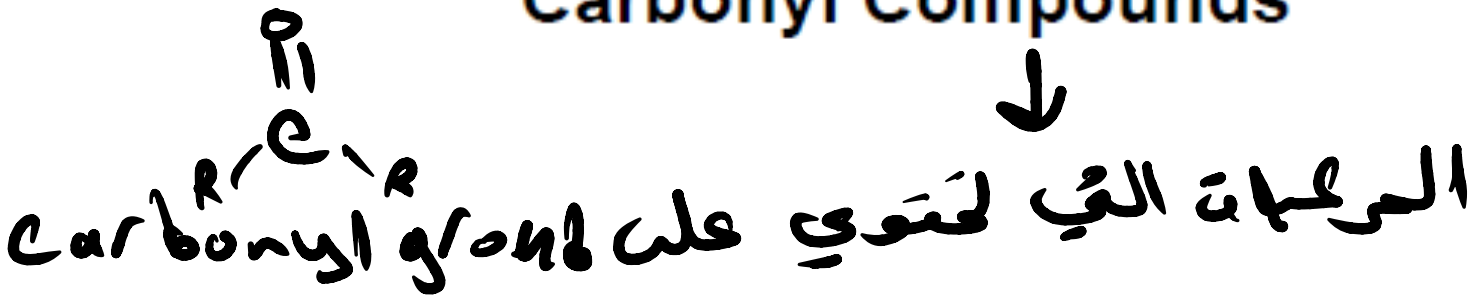
Calculate the λ_{max} for the compound

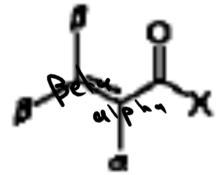


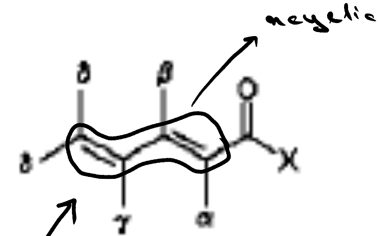
Solution

Base value	**253 nm**
2 Extended double bonds (2x30)	**60 nm**
5 Ring residues (5x5)	**25 nm**
1 Exocyclic double bond (1x5)	**5 nm**
Calculated λ_{max}	**343 nm**
Observed	**345 nm**

Woodward's Rules for Conjugated Carbonyl Compounds







Base values:

X = R	
Six-membered ring or acyclic parent enone	λ=215 nm
Five-membered ring parent enone	λ=202 nm
X = H	λ=208 nm
X = OH, OR	λ=195 nm

Increments for:

Double bond extending conjugation		30
Exocyclic double bond		5
Endocyclic double bond in a 5- or 7-membered ring for X = OH, OR		5
Homocyclic diene component		39
Alkyl substituent or ring residue	α	10
	β	12
	γ or higher	18

Polar groupings:

-OH	α	35
	β	30
	δ	50
$-OC(O)CH_3$	α,β,γ,δ	6
$-OCH_3$	α	35
	β	30
	γ	17
	δ	31
-Cl	α	15
	β,γ,δ	12
-Br	β	30
	α,γ,δ	25
$-NR_2$	β	95

*Solvent shifts for various solvents:

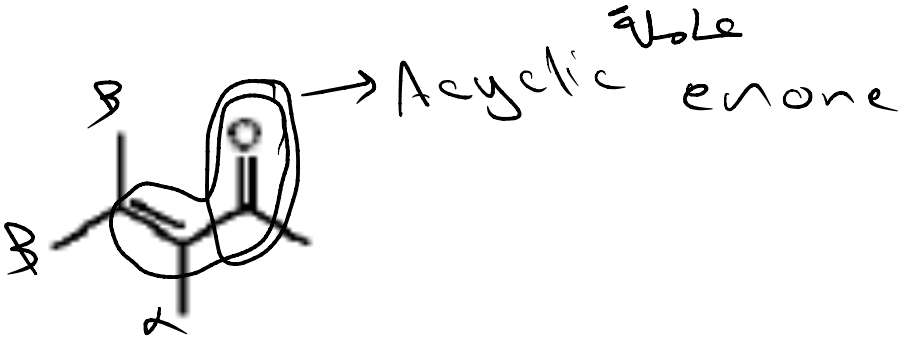
Solvent	λ_{max} shift (nm)
water	+ 8
chloroform	- 1
ether	- 7
cyclohexane	- 11
dioxane	- 5
hexane	- 11

polar + Hydrogen bonding solvents ← Red shift

blue shift

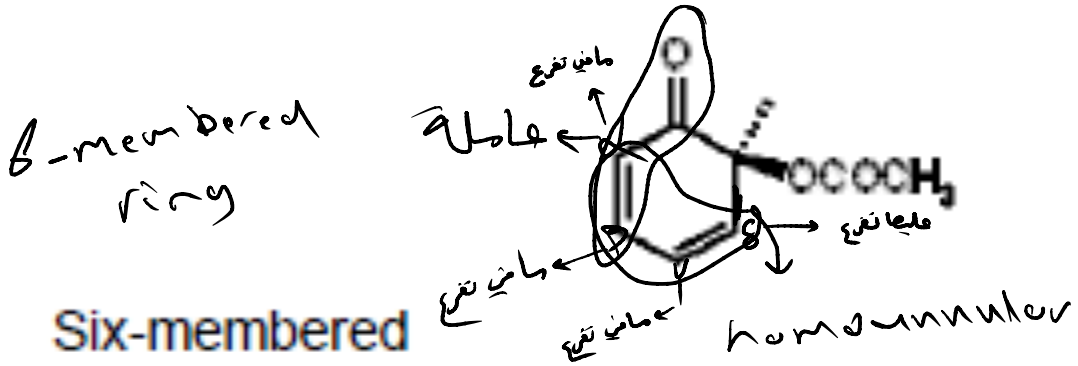
* كل التطبيقات على $\pi^* \rightarrow n$ و $\pi^* \rightarrow \pi$ لانه هم ليس إلى بالمحضم وبشوفهم بالاجهزة

example

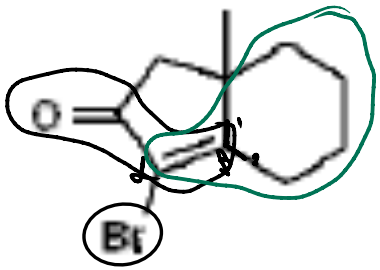


Acyclic enone:		215 nm
α-Alkyl groups or ring residues:		10 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Calculated:		249 nm
Observed:		249 nm

Five-membered ring parent enone:		202 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Exocyclic double bond:		5 nm
Calculated:		231 nm
Observed:		226 nm



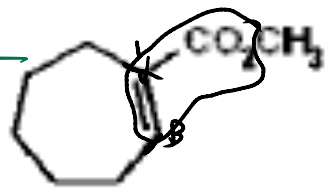
Six-membered ring or alicyclic parent enone:	215 nm
Extended conjugation:	30 nm
Homocyclic diene component:	39 nm
δ-Alkyl groups or ring residues:	18 nm
Calculated:	302 nm
Observed:	300 nm



Five-membered ring parent enone:		202 nm
α-Br:		25 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Exocyclic double bond:		5 nm
Calculated:		256 nm
Observed:		251 nm

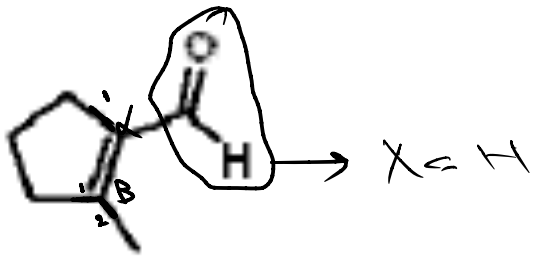
Carboxylic acid:	195 nm
α-Alkyl groups or ring residues:	10 nm
β-Alkyl groups or ring residues:	12 nm
Calculated:	217 nm
Observed:	217 nm

7 membered ring (X = OR)

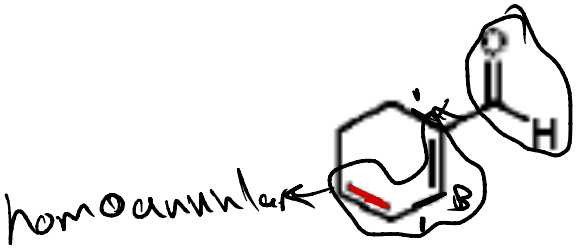


(C(=O)-O-CH3) — X = OR

Ester: C(=O)OR	195 nm
α-Alkyl groups or ring residues:	10 nm
β-Alkyl groups or ring residues:	12 nm
Endocyclic double bond in 7-membered ring:	5 nm
Calculated:	222 nm
Observed:	222 nm



Aldehyde:		208 nm
α-Alkyl groups or ring residues:		10 nm
β-Alkyl groups or ring residues:	2 x 12 =	24 nm
Calculated:		242 nm
Observed:		242 nm



Aldehyde:	208 nm
Extended conjugation:	30 nm
Homodiene component:	39 nm
α-Alkyl groups or ring residues:	10 nm
δ-Alkyl groups or ring residues:	18 nm
Calculated:	304 nm
Observed:	302 nm