Calculation of λ_{max} of Organic Compounds Using Woodward Fieser Rules

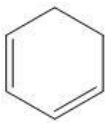
In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure. In 1959 Louis Frederick Fieser modified these rules with more experimental data, and the modified rule is known as Woodward-Fieser Rules. It is used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution of chromophore.

WOODWARD- FIESER RULES:

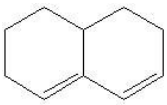
Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

I) CONJUGATED DIENE CORRELATIONS:

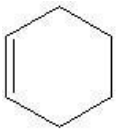
Homoannular Diene:- Cyclic diene having conjugated double bonds in same ring.



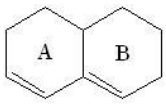
Heteroannular Diene:- Cyclic diene having conjugated double bonds in different rings.



Endocyclic double bond:- Double bond present in a ring.



Exocyclic double bond: - Double bond in which one of the doubly bonded atoms is a part of a ring



Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.

PARENT VALUES AND INCREMENTS FOR DIFFERENT SUBSTITUENTS/GROUPS:

I) CONJUGATED DIENE CORRELATIONS:

i) Base value for an unsubstituted, conjugated, homoannular diene = 253 nm

ii) Base value for an unsubstituted, conjugated, acyclic or heteroannular diene = 214 nm

Increments for:

Each extra double bonds in conjugation + 30 nm

Exocyclic double bond (effect is twofold if the bond is exocyclic to two rings) + 5 nm

Substituent effect:

A. -OCOR or –OCOAr + 0 nm

B. Simple alkyl substituents or ring residue + 5 nm

C. Halogen (-Cl, -Br) + 5 nm

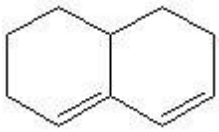
D. OR (R=Alkyl) + 6 nm

E. SR (R=Alkyl) + 30 nm

F. NR_2 (R=Alkyl) + 60 nm

Eg:

1.

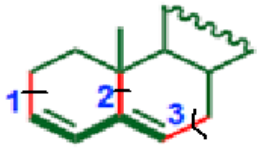


Base value = 214 nm
Ring residue = 3 x 5 = 15 nm

Exocyclic double bond = 1 x 5 = 5 nm

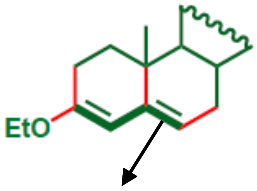
λ_{max} = 214 + 15 + 5 = 234 nm

2.



base value : 214 nm
3 ring residues : +15
1 exocyclic C=C : + 5 .
Total λ_{max} : 234 nm
Observed : 235 nm

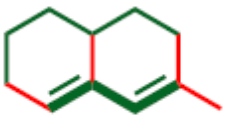
3.



Exocyclic double

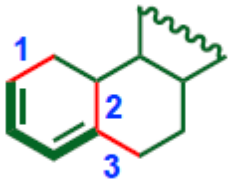
base value :214 nm
3 ring residues : +15
1 exocyclic C=C : + 5
-OR : + 6 .
Total λ_{max} : 240 nm
Observed : 241 nm

4.



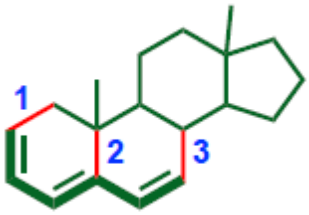
Base value : 214 nm
3 Ring residues : +15
1 Alkyl substituent: + 5
1 Exocyclic C=C : + 5.
Total λ_{max} : 239 nm

5.



base value (Homoannular) : 253 nm
3 ring residues : +15
1 exocyclic C=C : + 5
Total λ_{max} : 273 nm (Observed : 235 nm)

6.



base Value: 253 nm
3 Ring residues: +15
1 Exocyclic C=C: + 5
Double-bond Extending Conjugation: +30 .
Total λ_{max} : 303 nm
Observed: 304 nm

7.

Base value: 214 nm

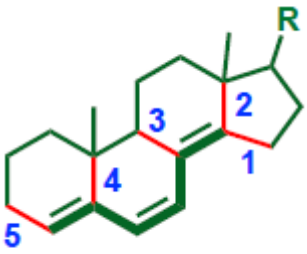
2 Ring residue +10
Exocyclic C=C: + 5
Total λ_{max}: 229 nm

Observed: 230 nm

8.

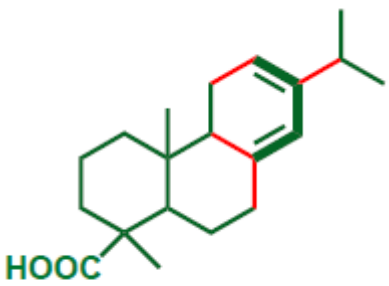
Base value: 214 nm
2 Ring residue: +10
Exocyclic C=C: + 5 .
Total λ_{max} 229 nm
Observed: 236 nm

9.



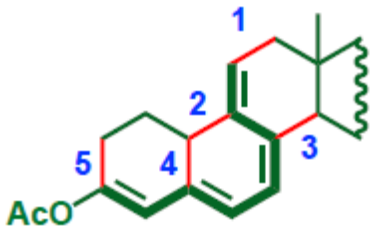
Transoid (base): 214 nm
5 ring residues: +25
1 DEC: +30
3 exocyclic C=C +15 .
Total λ_{max}: 284 nm
Observed: 283 nm

10.



Cisoid (base): 253 nm
3 ring residues: +15
1 Alkyl subs: +5
1 exocyclic C=C +5.
Total λ_{max}: 278 nm
Observed: 275 nm

11.



Cisoid (base): 253 nm
5 ring residues: +25
2 DEC: +60
3 exocyclic C=C +15 .
Total λ_{max}: 353 nm
Observed: 355 nm

II) ENONE:

Rules of Enon & Dienone Absorption
Base values:

i. Acyclic α,β-unsaturated ketones 215 nm
ii. 6-membered cyclic α,β-unsaturated ketones 215 nm
iii. 5-membered cyclic α,β-unsaturated ketones 202 nm
iv. α,β-unsaturated aldehydes 210 nm
v. α,β-unsaturated carboxylic acid & esters 195 nm

Increments for:

Double bond extending conjugation (DEC): +30

Exocyclic double bond: + 5

Homodiene component: +39

Increments for:

Alkyl group/ring residue: α position +10, β position +12, γ & higher position +18

Polar groups:

-OH: α position +35, β position +30, δ position +50

-OAc: α, β, γ + 6

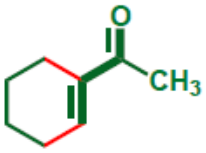
-OMe: α +35, β +30 γ +17 δ +31

-SAlk: β +85

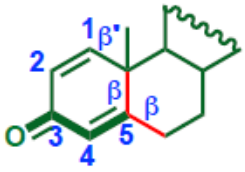
-Cl: α +15 β +12

-Br: α +25 β +30

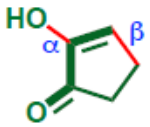
-NR_2: β +95



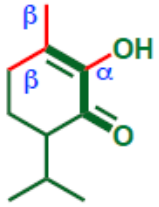
Base value:	215 nm
α substituent:	+10
β substituent:	+12
Total:	237 nm
Observed:	232 nm



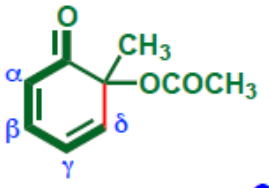
$\Delta^{4,5}$ system (base):	215 nm
2 β substituents:	+24
1 exocyclic C=C:	+ 5
Total:	244 nm
Observed:	245 nm



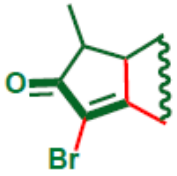
Base value:	202 nm
β substituent:	+12
α-OH:	+35
Total:	249 nm
Observed:	247 nm



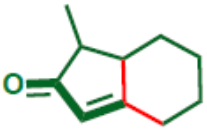
Base value:	215 nm
2 β substituents:	+24
α-OH:	+35
Total:	274 nm
Observed:	270 nm



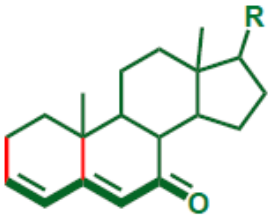
Base value:	215 nm
1 DEC:	+30
Homocyclic diene:	+39
δ ring residue:	+18
Total:	302 nm
Observed:	300 nm



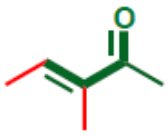
Base value:	202 nm
1 α-Br:	+25
2 β-ring residue:	+24
Exocyclic C=C:	+ 5
Total:	256 nm
Observed:	251 nm



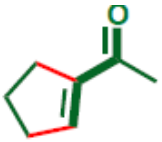
Base value:	202 nm
Exocyclic C=C:	+ 5
2 β-ring residues:	+24
Total:	231 nm
Observed:	226 nm



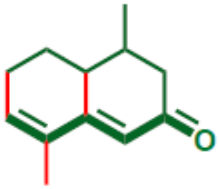
Base value:	215 nm
1 DEC:	+30
β-ring residue:	+12
δ ring residue:	+18
2 Exocyclic C=C:	+ 5
Total:	280 nm
Observed:	280 nm



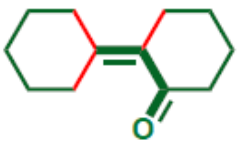
Base value:	215 nm
α alkyl substituent:	+10
β alkyl substituent:	+12
Total:	237 nm



Base value:	215 nm
α alkyl:	+10
β alkyl:	+12
Total:	237 nm



Base value:	215 nm
1 DEC:	+30
Exocyclic C=C:	+ 5
β-alkyl substituent:	+12
γ-alkyl substituent:	+18
δ-alkyl substituent:	+18
Total:	298 nm



Base value:	215 nm
1 α-alkyl:	+10
2 β-alkyl:	+24
2 Exocyclic C=C:	+10
Total:	259 nm