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Woodward Fisher Regulation for Calculating Absorption Maxima

Dhammadip C. Nandgaye[1], Abhijit N. Daf[2], Mr. Upadesh B. Lade[3], Mr. Durgesh W. Moharkar[4]

[1,3]Chhatrapati Shivaji College of Pharmacy, Deori

[4]Bajiraoji Karanjekar college of Pharmacy, Sakoli

[2]Agnihotri College of Pharmacy, Wardha.

ABSTRACT

Woodward regulations are countless units of empirically derived guidelines which try to predict the wavelength of the absorption most λmax in an ultraviolet-visible spectrum of a given compound. Inpute used in the calculation are the kind of chromophores present, the auxochromes substituents on the chromophores, and solvent. Example is conjugated carbonyl compound conjugated dienes, and polyenes. One set of Woodward-fishers policies for dienes is outlined is both homoannular with each double bonds contained in one ring or heteroannular with double bonds disbursed between two rings. With the useful resource of these regulations the UV absorption most can be predicted

KEYWORDS: Conjugated Dienes, Polyenes, α, β-Unsaturated Carbonyl Compounds

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1. INTRODUCTION

As we recognize that the presence of auxochrome or extension of chromophore may motive the alternative in wavelength and the depth of the absorption maximum. Woodward and fisher formulated a hard and fast of empirical regulation which will be used to predict absorption maxima of conjugated system like dienes, enones, aromatic structure (benzene and its derivative), benzoyl compounds and so forth.

2. WOOD WARD FISHER RULE

In 1945 Robert Burns Woodward gave positive guidelines for correlating λmax with molecular structures. In 1959 Louis Frederick Fisher changed these rule with extra experimental data, and the modified rule is referred to as Woodward-fisher Rule. It is used to calculate the position and λmax for a given structure via touching on the sort of chromophores digit, the substituents at the chromophore, and shift due to solvent. According to Woodward's regulations the λmax of the molecule can be calculated using a formula:

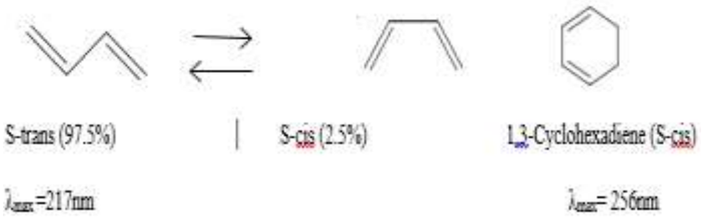
λ_{max} = Base value + ∑ substituent contributions + ∑ other contribution

3. WOODWARD FISHER RULE FOR CONJUGATED DIENES OR POLYENES

Each sort of dienes or trienes device is having a sure fixed value of λmax that is called base value or parent value. The base value depends upon whether the dienes is a linear or heteroannular or transoid dienes, or whether its miles a cyclic or homo annular dienes. Substituents along with alkyl substituents or ring residue, double bond extending conjugation with businesses such as –Cl, Br and so on additionally a selected compound. A diene can be acyclic diene, homo-annular conjugated diene, and heteroannular diene.

1. Acyclic Dienes

An acyclic dienes exists in the main in s-trans (transoid) conformation as shown inside the case of butadiene. As acyclic diene can rotate approximately their unmarried bond to offer either cisoid or transoid, consequently they exist in Trans shape due to the excessive stability of the later. When this diene becomes a part of a ring machine as in 1, 3 cyclohexadiene, it's miles forced right into cisoid configuration. The wavelength of absorption is also shifted to longer wavelength and depth is decreased in evaluation with acyclic diene. The absorption maxima for 1, 3 cyclohexadiene is 256nm while 1, 3-butadiene shows λmax at 217nm

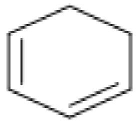


2. Cyclic Dienes

Cyclic dienes may be classified two classes depending upon whether the double bonds are in the equal ring.

a) Homo-Annular Conjugation Dienes:

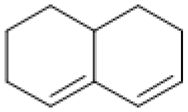
Both conjugated double bonds are inside the same ring and are having s-cis (cisoid) configuration. The s-cis configuration stress which will increase the power of floor nation, even as the electrical energy of the excited country is highly unchanged as a result the transition energy is decreased ensuing absorption at longer wavelength



e = 12000-28000 base λ_{max} = 253

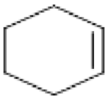
b) Hetero-Annular Dienes:

Conjugated double bonds are located in one of a sort jewelry and functions traces configuration the homo-annular dienes resemble with 1, 3- cyclohexadiene, whereas hetero-annular dienes with butadiene's

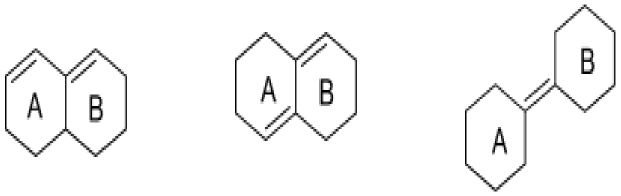


e = 5000 – 15000 base λ_{max} = 214

c) Endocyclic double bond: Double bond is present inside the ring.



d) Exocyclic double bond: double bond projecting outside the ring is called as exocyclic double bond.



e) Empirical Rule For Dienes

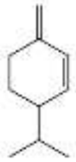
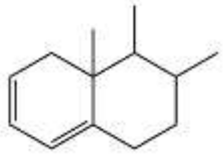
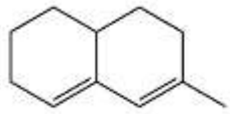
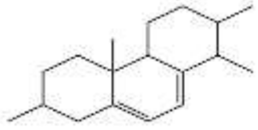
Base value for homo annular (cisoid) diene = 253nm

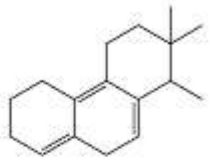
Base value for hetero annular (transoid) diene = 214nm increase for

a. Alkyl substituent or Ring residue connected to discern diene = 5nm
b. Double bond extending = 30nm
c. Exocyclic double bonds = 5nm
d. Polar substituent's
  I. –$OCOCH_3$ = +0
  II. –OR = +6
  III. –SR = +30
  IV. –Cl, Br = +5
  V. –NR_2 = +60

With the help of that regulation the UV absorption most λ_{max} can be anticipated for any alkene compound.

Table 01. UV absorption λmax for alkene and cyclic dienes compounds.

Sr. No.	Structure	Calculated λ_{max}
1		Base value = 214 2 alkyl group = 2*5 = 10 1 exocyclic bond = 1*5 = 5 Thus λ_{max} = 229nm
2		Base value = 253(homoannular) 3 ring residues = 3*5 =15 1 exocyclic bond = 1*5= 5 Thus λ_{max}= 273nm
3		Base value 214 (heteroannular) 4 ring residues = 4*5=20 1 exocyclic bond = 1*5=5 Thus λ_{max} = 273nm
4		Base value = 253 homoannular 4 ring residues = 4*5=20 2 exocyclic bond= 2*5=10 Thus λ_{max} = 283

5		Base value = 253 homoannular 6 ring residues =6*5=30 2 exocyclic bond = 2*5=10 1 double bond exocyclic to two rings = 2*5=10 1 double bond extending conjugation = 1*30=30 Thus λ_{max} = 333nm

The polyenes with extra than four conjugated double bond, Fisher-Kuhn rule is used to calculated λ_{max}.

Fisher Kuhn derived the subsequent equation to calculate the wavelength of most absorption λ_{max} and also maximum absorptive €max

λmax = 114+5x+y (48.0-107y)-16.5 Rendo-10Rexo

Where

λmax is the wavelength of most absorption

X is the wide varity of alkyl substituent or ring residues in the conjugated system

Y is the quantity of conjugated double bonds

Rendo is the number of ring with endo-cyclic double bond inside the conjugated machine

Rexo is the wide variety of ring exocyclic double bond in the conjugated device

Emax = (1074 * 104) y

Where

Emax is the maximum absorptivity

Y is the variety of conjugated double bond we can use this equation to calculate wavelength of most absorbance and the most absorptivity for polyenes such as β-carotene, Lycopene and so on.

Let us take β-carotene as an instance. The observed λmax of β-carotene is 452nm, at the same time as the discovered €max is 15.2 * 104 .

Structure

B-carotene, λ_{max} = 454nm

X (no. of alkyl substituent) = 10

Y (wide variety of conjugated double bond) = 11

Rendo (variety of endocyclic double bond) = 2

Rexo (wide variety of exocyclic double bond) = 0

Thus λmax = 114 + 5x + y(48.0 - 1.7y) – 16.5 Rendo - 10Rexo

= 114 + 5(10) + 11(48.0 - 1.7(11)) - 16.5(2) - 10(0)

= 114 + 50 + 11(29.3) – 33 – 0

= 114 + 50 + 322.3 – 33

= 453.30nm

Emax = (1.74 * 104)y

= (1.74 * 104) 11

= 19.14 * 104

4. WOODWARD FISHER RULE FOR ALPHA, BETA- UNSATURATED CARBONYL COMPOUND

Carbonyl compound have indispensable UV radiation, the allowed π to π^* transitions and the forbidden n to π^* transition. In amide, acids, esters or acid halides, the substituents viz. NR2, OH, OR, or –X on carbonyl team exhibit cited hypsochromic have an effect on at the n to π^* transition. The hypsochromic impact is due to the fact of inductive impact of nitrogen, oxygen or halogen atoms. The heteroatom withdraws electrons from carbonyl and makes carbonyl oxygen lone pair of electrons increased stabilized due to its involvements in developing C=O bond order. As a result, the n to π^* transition of these compounds is shifted to 200-215nm vary relative to 270nm in aldehydes and ketones. Conjugated of the carbonyl organization with double bond shift each n to π^* and π to π^* transition to longer wavelength. The result on π to π^* band is extra reporte. Woodward formulated guidelines to waiting for the vicinity of an absorption most in an unknown enone. These regulations have been summarized beneath

Base value for

a. Acyclic α, β unsaturated ketones =215nm
b. 6 membered cyclic α, β unsaturated ketones =215nm
c. 5 membered cyclic α, β unsaturated ketones =202nm
d. α, β unsaturated aldehydes =210nm
e. α, β unsaturated carboxylic acid and esters =195nm

Increment for

i. Each double bond extending conjugation =30nm
ii. Exocyclic double bond =5nm
iii. Homo-annular dienes component =39nm

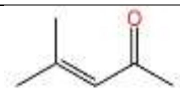
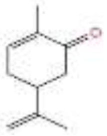
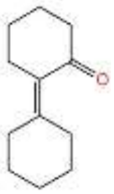
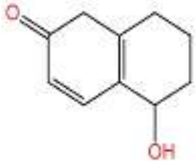
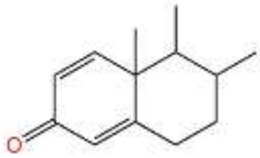
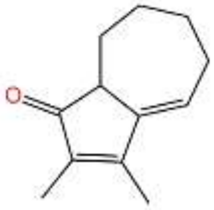
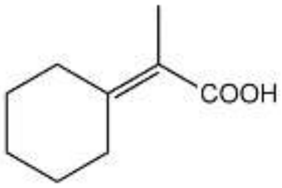
Table 02. Substituents base value for carbonyl compounds

Substituents	α-position	β-position	γ-position	δ-position
Each alkyl substituent ring residues	10nm	12nm	18nm	18nm
-OH	35nm	30nm	50nm	50nm
-OAc	06nm	06nm	06nm	06nm
-OMe	35nm	30nm	17nm	31nm

-Cl	15nm	12nm	12nm	12nm
-Br	25nm	30nm	25nm	25nm
-SR	-	85nm	-	-
-NR_2	-	95nm	-	-

Since carbonyl compoosites are polar in nature, the position of immersion bands calculate on the detergent used. Hance solvent correlations are needed to calculate the λmax values. All the below correlation are taken in ethanol as detergent. For calculating λmax in different detergents, one ought to correspond of solvent corrections.

Table 03. UV absorption λmax for Carbonyl Compounds

Sr. No.	**Structure**	**Calculated λmax**
1		Base value =215 2β-alkyl substituent =2x12=24 Calc. λmax= 239nm
2		Base value =215 1α-substituent =1x10=10 1β-alkyl substituent =1x12=12 Calc. λmax =237nm
3		Base value =215 1α-substituent =1x10=10 2β-alkyl substituent =2x12=24 1 double bond exocyclic to 2 ring =2x5=10 Calc. λmax =259nm
4		Base value =215 1γ-substituent= 1x10=10 2δ-alkyl substituent =2x18=36 1 double bond extending conjugation =1x30=30 1 homoannular diene system =1x30=30 Calc. λmax= 338nm
5		Base value =215 2β-ring residue =2x12=24 1 exocyclic double bond =1x5=5 Calc. λmax =244nm
6		Base value =202 1α-substituent =1x10=10 1β-alkyl substituent =1x12=12 1γ-ring residues =1x18=18 1δ-ring residues =1x18=18 1 double bond extending conjugation =1x30=30 1 exocyclic double bond =1x5=5 Calc. λmax =295nm
7		Base value =215 1β-alkyl substituents = 1x12=12 1β- ring residues = 1x12=12 1α-OH substituents = 1x35= 35 Calc. λmax = 274nm
8		Base value = 195 1α- substituents =1x10=10 2β- ring residues =2x12=24 1 exocyclic double bond = 1x5=5 Cal. λmax = 234nm

5. OPERATIONS OF UV- VIS SPECTROSCOPY.

UV-visible spectroscopy is a fashion that readily allows one to determine the attention of substances and thus enables scientists to study the rates of responses, and determine rate equations for responses, from which a medium can be proposed. As similar UV spectroscopy is used considerably in tutoring, exploration and logical laboratories for the quantitative analysis of all motes that absorb ultraviolet and visible electromagnetic radiation.

- Quantitative analysis UV-visible spectroscopy has been exploited for the structure explication of organic composites, discovery of different organic composites present in a admixture and their separation by several logical ways similar as thin subcast chromatography.

a. Structure explication of organic composites UV spectroscopy is useful in the structure explication of organic composites. The presence or absence of a particular immersion band at a particular wavelength may be regarded as an substantiation for the presence or absence of a particular chromophore in the emulsion.

b. Determination of the contamination TLC is a varitably simple fashion and is generally used for the qualitative analysis of the response admixture. Numerous organic compound absorb UV light of colorful wavelengths. This can be used for the determination of contaminations in organic composites.

6. SUMMARY

1. In this module we’ve seen that the UV- vis spectroscopy have come the most important logical tool in the ultramodern day laboratory due to its simplicity, versatility, speed, delicacy and cost-effectiveness.
2. We come to know about the Woodward Fisher rule and its connection in calculating the immersion maxes for several functional groups.
3. How the substituents affect the immersion pattern in benzene and other monoor di-substituted benzenes.
4. We’ve seen different operation of UV spectroscopy qualitatively as well as quantitatively.

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