Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Second Year)

Subject: Chemistry

Course Code: CHC103

Course Title: Physical and Organic Chemistry (Section B)

Unit: UV-Visible Spectroscopy in Organic Chemistry

Module Name: Woodward - Fieser Calculations of λmax : Conjugated Dienes

Name of the Presenter: Dr. Mira V. Parmekar

Notes

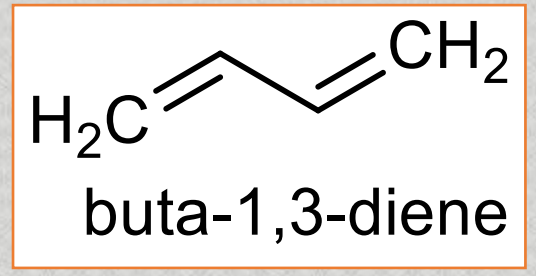
Introduction

- In 1945 Robert Burns Woodward gave certain rules for correlating λ_{max} with molecular structure which in 1959, were modified by Louis Frederick Fieser with the help of more experimental data.
- These modified rules are 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.

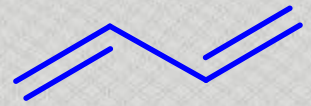
Woodward – Fieser Rules

Each diene or triene system has 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 this basic value to obtain λ_{max} for a particular compound.

Terminology

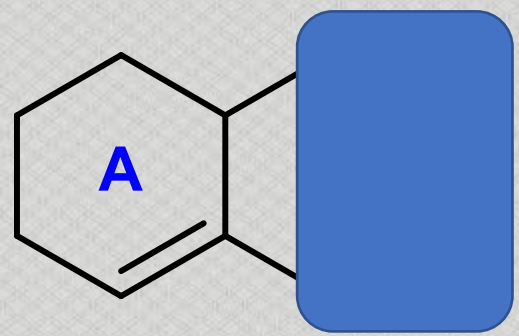


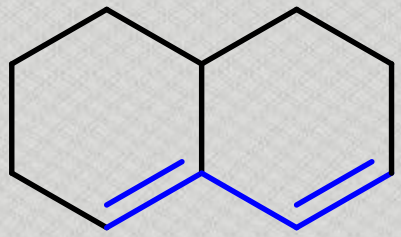
buta-1,3-diene



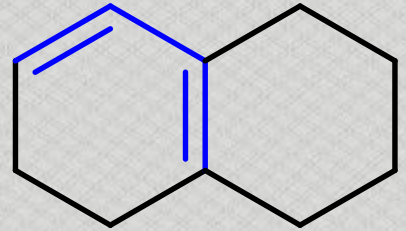
S-trans

S-cis





Heteroannular diene



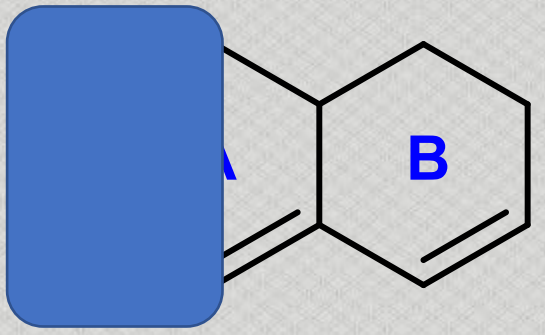
Homoannular diene

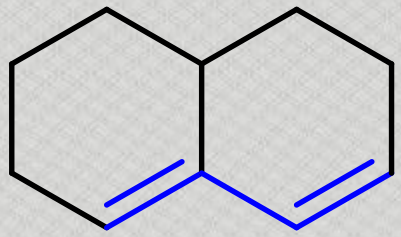
Endocyclic double bond

Terminology

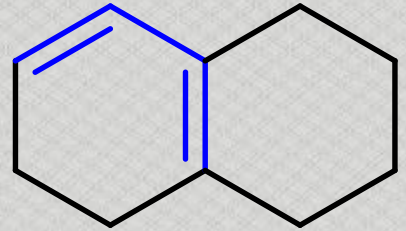
S-trans

S-cis



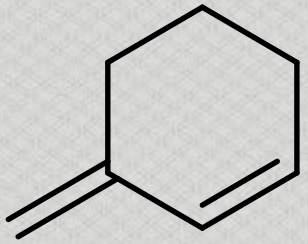


Heteroannular diene



Homoannular diene

Endocyclic double bond

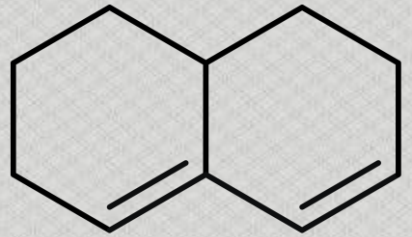


Exocyclic double bond

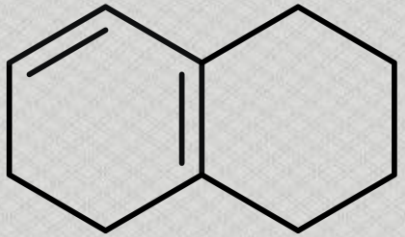
Base Values → Chromophores

1,3-butadiene → 217 nm

Acyclic /



Heteroannular diene → 214 nm

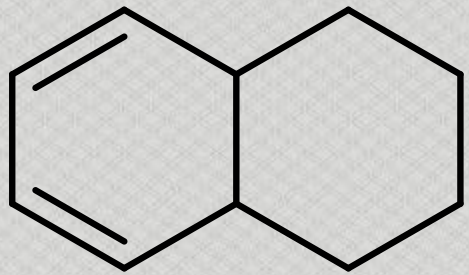


Homoannular diene → 253 nm

Increments → Auxochromes

Ring residue	+ 5 nm
Alkyl substituent	
Exocyclic double bond	
-Cl, -Br	
-OAlkyl group	+ 6 nm
Extended conjugation	+ 30 nm
Secondary amine	+ 60 nm

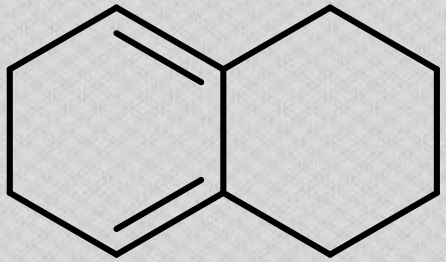
Example 1



Base value	→	+ 253 nm
Ring residue	→	+ 10 nm
Exocyclic double bond	→	+ 0 nm
Extended conjugation	→	+ 0 nm
Alkyl substituent	→	+ 0 nm

$$\lambda_{max} = 263 \text{ nm}$$

Example 2



Base value	→	+ 253 nm
Ring residue	→	+ 20 nm
Exocyclic double bond	→	+ 10 nm
Extended conjugation	→	+ 0 nm
Alkyl substituent	→	+ 0 nm

$$\lambda_{max} = \underline{\underline{283\ nm}}$$

Summary

- **Robert Burns Woodward and Louis Frederick Fieser gave certain rules for correlating λ_{max} with molecular structure known as Woodward-Fieser Rules, used to calculate the position and λ_{max} for a given structure by relating the position and degree of substitution.**
- **Each conjugated system has a certain fixed value at which absorption takes place. The contribution made by various substituents or ring residue, etc. added to this basic value to obtain λ_{max} for a particular compound.**
- **Extended conjugation always results in Bathochromic shifts.**