IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)
An International Open Access, Peer-reviewed, Refereed Journal

A Review On Woodward Fisher Regulation For Calculating Absorption Maxima

1. **Research Scholar: Yashika Gupta**
2. **Co-author: Jitendra kr. Yadav, Associate Professor, S.N. College of Pharmacy.**

Abstract

Woodward regulations consist of many units based on empirical guidelines that aim to estimate the absorption wavelength, specifically λmax, within the ultraviolet-visible spectrum for a particular compound. Factors considered in the calculations include the types of chromophores, the substituent auxochromes on those chromophores, and the solvent used. Examples of this include conjugated carbonyl compounds, conjugated dienes, and polyenes. For dienes, one set of Woodward-Fischer rules distinguishes between homoannular systems, where double bonds are found within a single ring, and heteroannular systems, where double bonds are spread out across two rings.

Keywords- Auxochromes, λmax, α, β-Unsaturated Carbonyl Compounds.

Introduction

The Woodward-Fieser rules are practical guidelines that help forecast the ultraviolet (UV) absorption peaks of conjugated organic compounds. By following these rules, one can systematically estimate the wavelength at which a compound absorbs the most, taking into account its structure and any substituents. Every diene or triene has a specific value where absorption occurs, known as the Base value or Parent value. To determine the λmax for a specific compound, we add the influences from different alkyl groups, ring structures, extended double bond conjugation, and polar groups like –Cl and –Br to this basic value.

The highest wavelength of light absorption (max) for a conjugated organic compound can be determined by applying the Woodward-Fieser criteria. The molecule's chromophores and auxochromes influence the kind, location, and count of these rules.

WOODWARD FISHER RULE

Woodward's rules, which honor Robert Burns Woodward and are also referred to as the Woodward–Fieser rules in recognition of Louis Fieser, consist of various sets of rules based on empirical data. These rules aim to estimate the wavelength of the maximum absorption (λmax) in the UV-Vis spectrum of a specific compound. Factors that contribute to this calculation include the kinds of chromophores present, the auxochromes (which are substituents on the chromophores), and the solvent used. Some examples of these compounds include conjugated carbonyl compounds, conjugated dienes, and polyenes. We understand that having an auxochrome or extending a chromophore can influence changes in wavelength and the absorption maximum's depth. Woodward and Fischer created a set of rules that can help us predict the absorption maxima in conjugated systems such as dienes, enones, aromatic structures (including benzene and its derivatives), benzoyl compounds, and more.

Key aspects of the Woodward-Fieser rules:

Chromophores are linked groups within molecules that impart color by absorbing visible light. Some examples of chromophores include double bonds, carbonyl groups, and aromatic rings.

1. ***Base Values:***
   Each kind of conjugated system, whether it be a homoannular diene, a heteroannular diene, or an α,β-unsaturated ketone, has its own set base value for λmax.
2. ***Substituent Effects:***
   The base value is adjusted based on the impact of different substituents such as alkyl groups, halogens, and oxygen-containing parts, along with other structural elements like exocyclic double bonds and extended conjugation.
3. ***Conjugation:***
   The degree of conjugation, which refers to the number of alternating single and double bonds, plays a crucial role in determining λmax; more conjugation results in absorption at longer wavelengths.
4. ***Solvent Effects:***
   The type of solvent used for the measurement can also affect λmax, especially polar solvents, which usually lead to a small shift in absorption.

Woodward-Fieser Rules for Calculating the lambda max of Conjugated Dienes and Polyenes.

Every type of diene or triene has a specific maximum wavelength, known as the base value or parent value. This base value varies depending on whether the diene is a linear, heteroannular, or transoid type, or if it is a cyclic or homoannular diene. Various substituents, such as alkyl groups or ring residues, as well as double bonds that enhance conjugation with elements like Cl and Br, also influence the value. A diene may be classified as acyclic, homoannular conjugated, or heteroannular.

Most organic compounds contain conjugated dienes and polyenes. A good example is the benzene ring, which qualifies as a conjugated polyene. Thus, understanding how to apply the Woodward-Fieser rules is important for determining the maximum absorption wavelength of these compounds.

Using Woodward's rules, you can find the Amax of a molecule through a specific formula:

$$\text{Amax} = \text{Base value} + \sum \text{Substituent Contributions} + \Sigma\ \text{Other Contributions}$$

The base value varies depending on the type of diene, such as whether it is linear, heteroannular, transoid, cyclic, or homoannular (more details on these types will follow). By adding all the substituent contributions to the base value, you can calculate the molecule's maximum absorption wavelength.

1. **Acyclic Dienes**
   Typically, acyclic dienes, such as butadiene, predominantly adopt the s-trans (transoid) conformation. These compounds can rotate around their single bonds, which allows them to exist in either cisoid or transoid forms. However, they are more stable in the trans configuration, making this form more common. When an acyclic diene is incorporated into a ring structure, like in 1,3-cyclohexadiene, it is forced into the cisoid arrangement. As a result, the absorption wavelength shifts to longer values, and the absorption intensity decreases compared to the acyclic

diene. Specifically, the absorption maximum for 1,3-cyclohexadiene is at 256 nm, while 1,3-butadiene shows an absorption maximum at 217 nm.

2. **Cyclic Dienes**

Cyclic dienes can be divided into two groups based on whether the double bonds are located within the same ring.

a. ***Heteroannular Diene / Transoid Diene or Linear Diene:***

This type of diene typically consists of two trans dienes linked together. The presence of trans double bonds results in a linear configuration, which is also referred to as a heteroannular diene, since it cannot be incorporated into a single ring structure without causing significant instability (rings with 5-6 carbons are usually the most stable, with a few exceptions). According to the Woodward-Fieser rules, the baseline value for a heteroannular diene system is 215 nm.

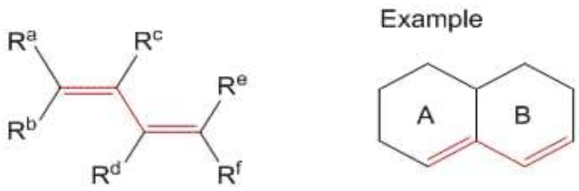


Fig. Examples of heteroannular dienes.

b. ***Homoannular diene / cisoid diene or cyclic diene:***

Is a type of diene formed by two cis dienes that are connected. Because the double bonds are on the same side, the molecule usually creates a circular structure, which is why it's referred to as a cyclic or homoannular diene. According to the Woodward-Fieser rules, the standard value for this diene system is 253 nm.

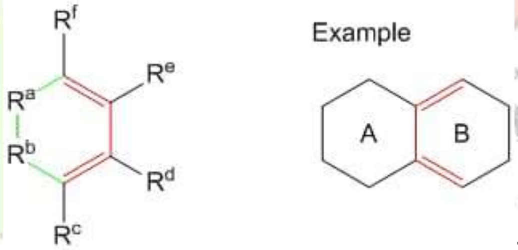


Fig. Examples of homooannular dienes.

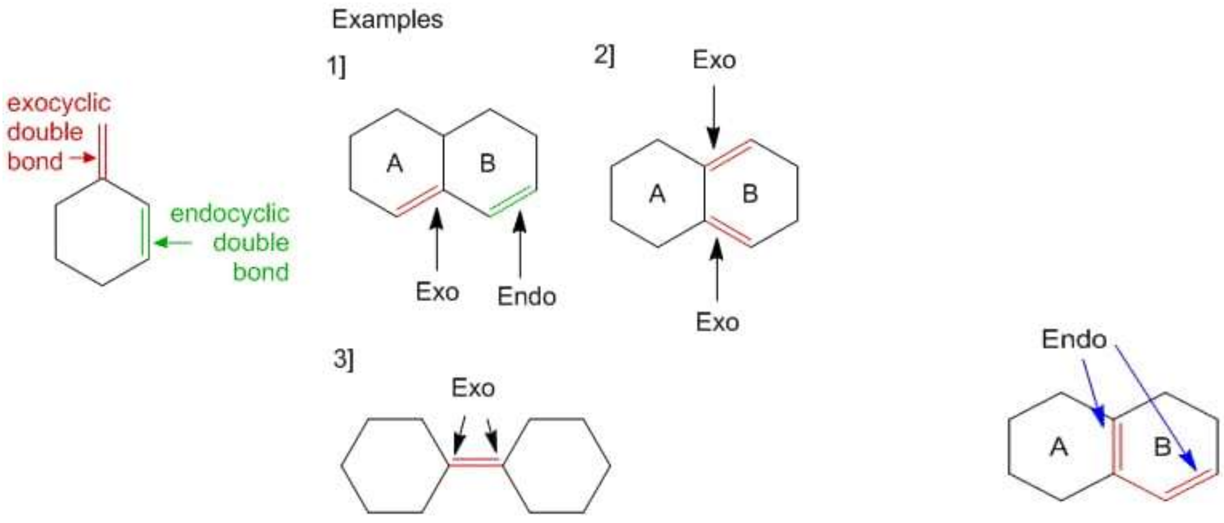
c. ***Other Contributors***

1. Exocyclic Double Bonds

An exocyclic double bond is defined as a double bond where one carbon atom is included in a ring, but the other carbon atom is not connected to that same ring. The term "exocyclic" suggests that the double bond exists outside the ring, whereas "endocyclic" refers to a double bond that occurs inside the ring.

2. Endocyclic Double Bonds

Double bonds that are found within two rings are referred to as endocyclic. Here, we provide an illustration of a double bond that shares carbon atoms between rings A and B. However, it is classified as endocyclic because, at any moment, the double bond is associated solely with one of the rings.



NOTE-

The diagram above distinguishes between double bonds that are exocyclic (marked in red) and those that are endocyclic (marked in green).

- In the first example, the double bond found in ring A is exocyclic to ring B because it connects to an atom that both rings share. Conversely, the double bond in ring B does not link to any atoms from ring A and is solely within its own ring, making it endocyclic.
- In the second example, both double bonds are located in ring B and link to shared carbon atoms with ring A, which means both double bonds are exocyclic.
- For the third example, there is one double bond that is exocyclic at two points, connecting to two separate rings. In this scenario, the overall impact would be 2 times + 5 nm (which totals + 10 nm).

Application of the Woodward-Fieser Rule

As previously mentioned, the Woodward-Fieser rule is commonly used to find the position of the absorption maxima (λmax). When this rule is applied to determine the λmax values for conjugated dienes and unsaturated ketones, the results may vary slightly from those actually observed, but it still provides a general idea of where absorption occurs.

- The Woodward-Fieser rules are practical guidelines that help predict the highest wavelength (λ max) of absorption in conjugated systems during UV-Vis spectroscopy.

Limitations of the Woodward-Fieser Rule

- However, the validity of the rule is compromised if there is distortion in the chromophore caused by ring strain or by additional conjugation not found at the ends of the chromophore.
- The Woodward rule yields accurate results for diene and carbonyl compounds mainly when there is no strain around the chromophore. It works well for acyclic compounds and typically for six-membered ring systems.
- The Woodward-Fieser rules are based on observed data and give rough estimates rather than precise numbers. Measured values can differ a bit from what is calculated.
- These rules might not work as well for complicated structures or those with many substitutions.

- When dealing with compounds that have over four conjugated double bonds, using the Fieser-Kuhn rule is usually better for getting a more precise result.
- Additionally, aspects such as solvent polarity and temperature can affect the λmax and should be taken into account for a thorough analysis.

Fieser-Kuhn Rules

The Woodward-Fieser guidelines are effective for conjugated systems containing fewer than four double bonds. When dealing with molecules that have more than four double bonds, the Fieser-Kuhn rules are necessary to calculate λmax. To understand how to apply these rules, take a look at our post on Fieser-Kuhn Guidelines for Calculating the Maximum Absorption Wavelength (Lambda-max) of Polyenes, which includes example problems.

REFERENCES:

1. Donald L. Pavia, Gary M. Lampman, Introduction To Spectroscopy 3rd edition, Thomson Learning, 2001, Ultraviolet Spectroscopy 366, 372-374.
2. William Kemp, Organic Spectroscopy 3 rd edition Palgrave, Houndmills, Basingstoke, 175 fifth Avenue, New York, 1991, Ultraviolet and visible spectroscopy 259-263.
3. KALSI P.S., "A Text Book Of Organic Spectroscopy", published by NEW AGE INTERNATIONAL PUBLISHERS, 6th edition. 2007. Pp. (40)
4. Donald L. Pavia, Gary M. Lampman, Introduction to Spectroscopy 5th edition, printed in the United States of America, 2009, Ultraviolet Spectroscopy 596-605.
5. Louis F. Fieser; Mary Fieser; Srinivasa Rajagopalan (1948). "Absorption Spectroscopy and the Structures of the Diosterols". J. Org. Chem. 13 (6): 800–6.
6. SHARMA Y.R., "Elementary Organic Spectroscopy", published by S. Chand & Company Ltd. edition, 2006. Pp. (31-49)
7. Silverstein, Robert M.; Webster, Francis X.; Kiemle, David J.; Bryce, David L. (2016) Spectrometric Identification of Organic Compounds, 8th Edition. Wiley.
8. Louis F. Fieser; Mary Fieser; Srinivasa Rajagopalan (1948). "Absorption Spectroscopy and the Structures of Diosterals J. Org. Chem. 13 (6): 800-6. doi:10.1021/j0011648003 PMID 18106021.
9. Woodward, Robert Burns (1941). "Structure and the Absorption Spectra of 0.ß-Unsaturated Ketones". J. Am. Chem. Soc. 63(4): 1123. doi:10.1021/ja01849a066.