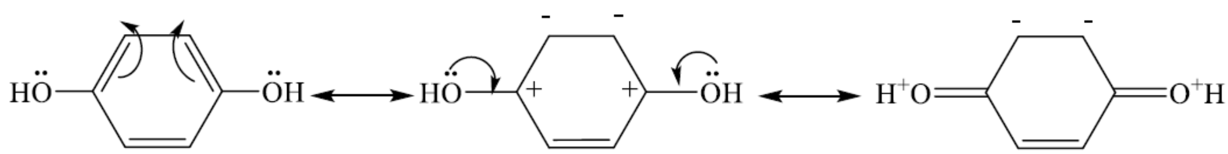
1-2-3-Substitution of two electron-donating groups:-

Substitution of two electron-donating groups at the para, meta, or ortho position, as shown in the following example:



It gives a shorter wavelength (higher energy) than substitution with two electron-withdrawing groups at any position. This is because electron-withdrawing groups contain double bonds that increase conjugation, which enhances resonance and lowers the energy required for electronic transition, resulting in a longer wavelength.

3-The effect of stereochemistry on ultraviolet–visible (UV–Vis) spectra:

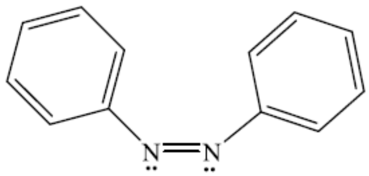
The effect of stereochemistry on ultraviolet spectra appears as an increase or decrease in wavelength. for example the compound 1,2-diphenylethene, which consists of two benzene rings and a double bond, existing in cis and trans forms.

Cis isomer
1,2-diphenylethene

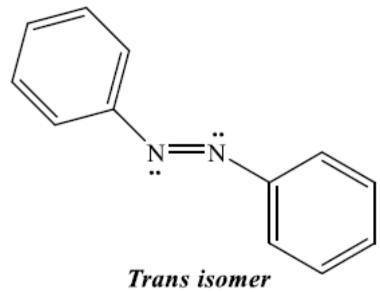
Trans isomer
1,2-diphenylethene

The cis isomer has a shorter wavelength than the trans isomer. This is because the cis isomer has greater steric hindrance, is less planar, and has less resonance. This increases the energy required for electronic transition, causing a decrease in wavelength.

Another example cis and trans 1,2- diphenylhydrazine.



Cis isomer
1,2-diphenyldiazene



Trans isomer
1,2-diphenyldiazene

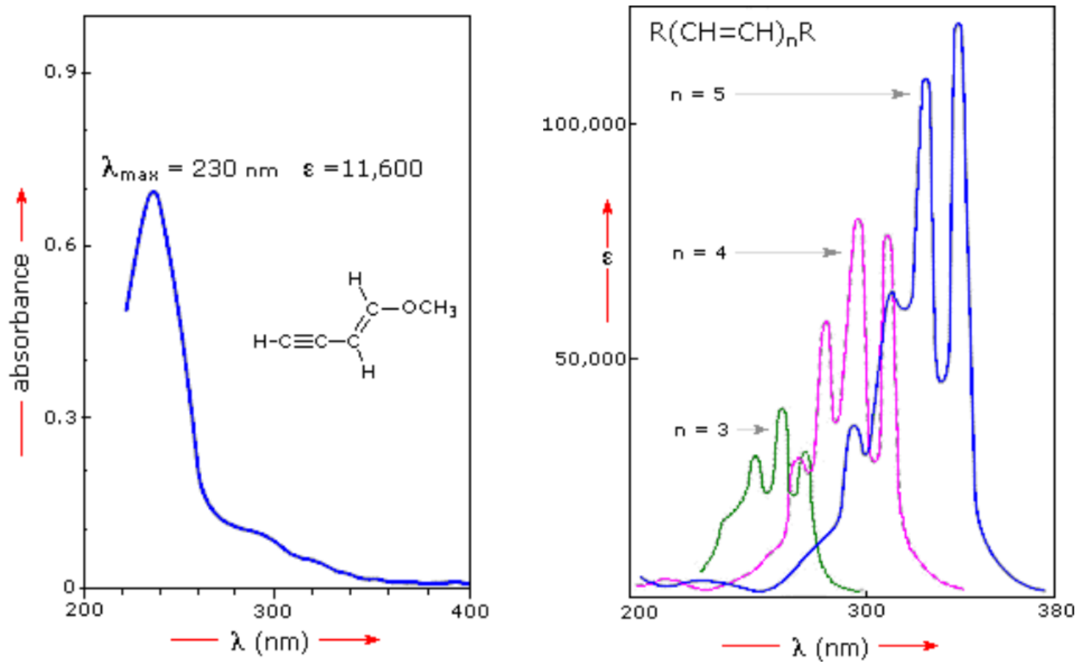
When comparing **1,2-diphenyldiazene** with **1,2-diphenylethene**, it is observed that 1,2-diphenyldiazene exhibits a higher wavelength than 1,2-diphenylethene.

The reason for this is the presence of a nitrogen atom in diphenyldiazene, which possesses an unshared pair of electrons (lone pair). This lone pair increases the electron density and enhances the resonance ability of the molecule. As a result, the energy required for the electronic transition decreases, leading to an increase in the absorption wavelength (bathochromic shift).

Factors that affect the position of absorption bands in the ultraviolet (UV) spectrum:

1- The effect of conjugation :

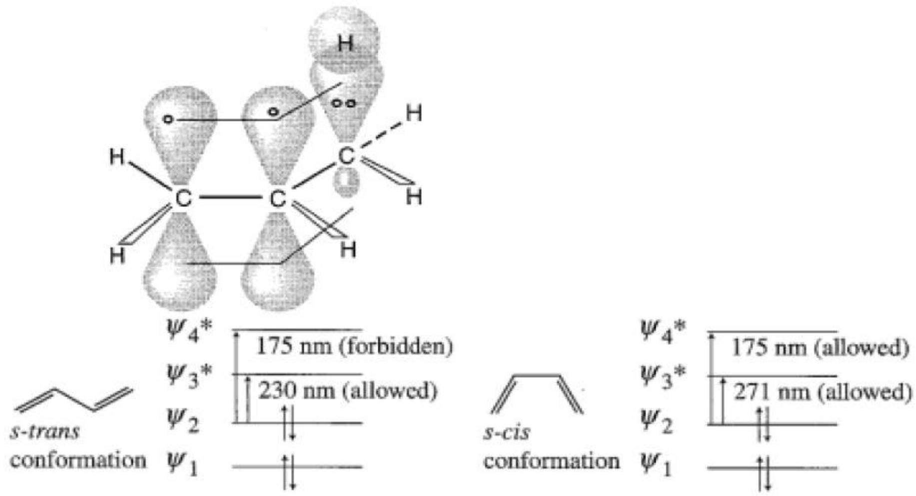
Comparison of the UV/Vis absorption spectrum of 1-butene, λ_{max} = 176 nm, with that of 1,3-butadiene, λ_{max} = 292 nm, clearly demonstrates that the effect of increasing conjugation is to shift toward longer wavelength (lower frequency, lower energy) absorptions

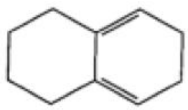


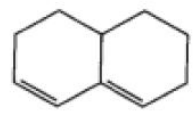
Terminology for Absorption Shifts

2- The effect of stereochemistry:

In the **cis** and **trans** configurations of butadiene, we observe that in the **trans** configuration the **π orbitals** lie in the same plane. Therefore, the molecule becomes planar, which facilitates better overlap between the **π orbitals**. In contrast, in the **cis** configuration the molecule is **non-planar** due to **steric hindrance**, which reduces the extent of orbital **overlap**. Whenever the overlap between orbitals decreases, the **energy required for the electronic transition increases**. Consequently, the absorption shifts to a **shorter wavelength** with **lower absorption intensity** compared with the **trans configuration**, where absorption occurs at a **longer wavelength (red shift)** because the orbitals lie in the same plane and overlap more effectively.







Homoannular diene (cisoid or *s-cis*)
Less intense, ε = 5,000–15,000
λ longer (273 nm)

Heteroannular diene (transoid or *s-trans*)
More intense, ε = 12,000–28,000
λ shorter (234 nm)

3- Effected of the solvents:

The selection of the solvent in **ultraviolet (UV) spectroscopy** is very important. One of the conditions for the solvent is that it **should not absorb in the same region where the substance being analyzed absorbs**. A solvent that **does not contain conjugated double bonds** is preferred so that it is **transparent in the UV region**. Examples of such solvents are shown in the following table:

Acetonitrile	190nm	n-Hexane	201nm
Chloroform	240	Methanol	205
Cyclohexane	195	Isooctane	195
1,4Dioxane	215	Water	190
95%Ethanol	205	Trimethyl phosphate	210

It is also preferable to use a **non-polar solvent** so that it **does not form hydrogen bonds with the solute**, unlike polar solvents which can form hydrogen bonds with the solute and lead to an **unclear or less accurate spectrum**.

Solvent shifts on the $n \longrightarrow \pi^*$ Transition of Acetone

Solvent	H_2O	CH_3OH	C_2H_5OH	$CHCl_3$	C_6H_{14}
λ_{max}	264.5	270	272	277	279

From the table we notice that water, which is a polar solvent, forms hydrogen bonds with the lone pair electrons on the oxygen atom in acetone (n). This stabilizes the ground state and reduces the wavelength, thereby increasing the energy required for the transition.

In contrast, hexane, which is a non-polar solvent, does not form hydrogen bonds with the n electrons, and therefore the absorption wavelength becomes longer, making it a better solvent for observing this transition.