

**Topic: Conjugation and Cross-conjugation**

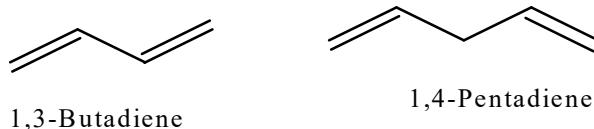
**Topics of discussion:**

- ☞ Conjugation
- ☞ Cross-conjugation
- ☞ Characteristics
- ☞ Examples

**Key points:**

**Conjugation**

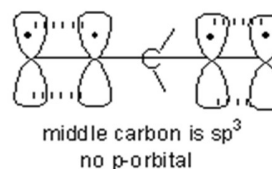
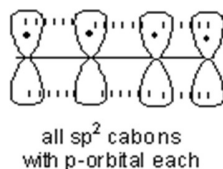
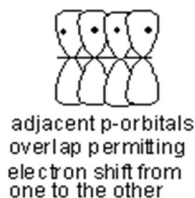
Presence of alternate double bonds in a molecule is considered as conjugation. The molecule is said to be conjugated. For example, 1,3-Butadiene is a conjugated diene, while 1,4-Pentadiene is not conjugated though it has two double bonds.



In conjugated diene, all carbons are  $sp^2$  hybridised while in non conjugated diene, the 3<sup>rd</sup> carbon is  $sp^3$  hybridized.

**Characteristics**

- In 1, 3-Butadiene all carbon atoms are  $sp^2$  hybridized. Hence they all have a p-orbital each and they are parallel to each other. p-orbitals on adjacent atoms overlap permitting electron movement from one to the other. In 1, 3-Butadiene an electron from one end of the molecule can move to the other end through the p-orbital pathway. This movement of electrons through the p-orbital pathway is one more way of describing conjugation.
- In 1,4-Pentadiene the carbon in the centre does not have a p-orbital therefore movement of electrons is not possible from one end of the molecule to the other. Hence it is not possible to draw resonance structures.
- In the following orbital pictures the p-orbital on adjacent atoms have been separated, but the understanding is that they overlap making electron movement possible. This is done so that the picture does not become confusing.



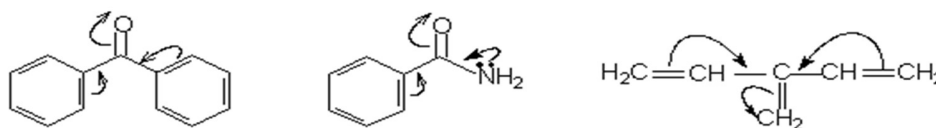
- A more conjugated compound absorbs light at higher  $\lambda_{max}$  in the UV-VIS range.

- As conjugation increases  $\lambda_{\max}$  increases, this is because in a more conjugated compound the energy required for transition of the electron from Highest Occupied molecular Orbital (HOMO) to the Lowest Unoccupied Molecular orbital (LUMO) decreases hence the wavelength of maximum absorption increases.
- Benzene does not absorb in the UV range only hence it is colorless to the human eye. Nitrobenzene has one more double bond in conjugation and its  $\lambda_{\max}$  increases and falls in the visible range and we are able to see it as yellow colored substance.

### Cross-conjugation

Cross-conjugation is a special type of conjugation in a molecule, when in a set of three Pi bonds only two pi-bonds interact with each other by conjugation, the third one is excluded from interaction. Whereas a normal conjugated system such as a polyene typically has alternating single and double bonds along consecutive atoms, a cross-conjugated system has a double-bonded unit single-bonded to one of the middle atoms of another conjugated chain. In classical terms, one of the double-bonds branches off rather than continuing consecutively: the main chain is conjugated, and part of that same main chain is conjugated with the side group, but all parts are not conjugated together as strongly.

When conjugation is possible from either end of the molecule towards the center it is called cross conjugation.



In cross conjugated compounds there are three groups generally present two of them are not directly in conjugation with each other while both of them are in conjugation with the third as seen in the following examples.

Acetamide is less basic than benzamide. In Benzamide ( $C_6H_5-CO-NH_2$ ), due to cross conjugation, lone pair of nitrogen is relatively free as  $>C=O$  group is in resonance with benzene ring as well whereas in acetamide ( $CH_3-CO-NH_2$ ), lone pair of nitrogen is more involved in resonance with  $>C=O$  group. Hence benzamide is more basic.

### Exercise

- Which of the following molecules is more conjugated and therefore has a higher  $\lambda_{\max}$ ?
  - 1,3-Butadiene or 1,4-Pentadiene
  - Chloroethene or propene
  - Benzene or Nitrobenzene
- Which of the following molecules are involved in cross conjugation?

