Year 2, Organic Chemistry, Chapter 04: Conjugation and Hyperconjugation

*Resonance/Delocalisation/Stability/Conjugation and Hyperconjugation/the Inductive and Mesomeric Effects/Activation and Deactivation all involve the **sharing** of electrons. Sometimes electron density is **increased** (e.g. '+M' or '+I') and at other times electron density (e.g. '-M' or '-I') is **decreased. The phrases "electron donating" and "electron withdrawing" are technically incorrect. In molecular species electrons are neither donated nor withdrawn, they are SHARED and ELECTRON DENSITY is thereby altered.***

- The translation of the Latin preposition "*con*" into English gives "with", and the Latin verb "*jugo*" means to join. "Conjugo" therefore means to join with – and "Conjugation" and "Hyperconjugation" are all to do with the wandering of/the leaching of an electron into an adjoining orbital.

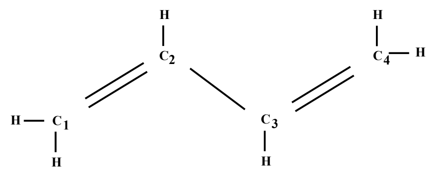
- **Conjugation and Hyperconjugation are in essence therefore all about delocalisation of electrons, and the most common usage of the term "Conjugation" is where it is applied to**
  - **the molecules of compounds that have alternating single and double bonds**
  - **where the unhybridised 'p' orbitals of the atoms in the main chain all lie in the same plane and** (if they have neighbouring atoms) **overlap each of their two immediately adjoining neighbouring unhybridised 'p' orbitals**
  - **and thus the electrons in all the continuous chain of unbonded overlapping unhybridised 'p' orbitals can become delocalised**
  - **thus conferring greater stability (that is associated with delocalisation) on the molecule.**

- That is a bit of a mouthful to swallow, but it is very easy to take in when actual examples are examined. Let us start by looking at Butadiene.

A Conjugated Molecule

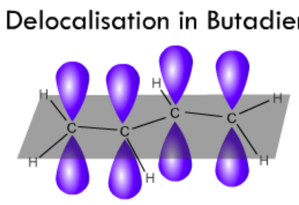
- All Carbon atoms must have four bonds. They are in Group IV therefore that is a given!

- However, if you look at a Butadiene[1] molecule, every single one of the C atoms is bonded to three other atoms therefore
  - they each form three s^1p^2 / sp^2 hybridised orbitals to form their three σ bonds, and
  - they each use an unhybridised 'p' orbital to form their π bonds.



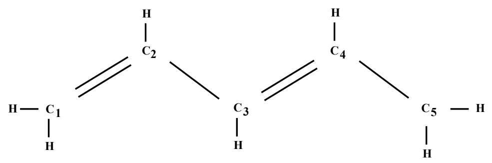
- As long as all four C atoms lie in the same plane, then each one of the four unhybridised 'p' orbitals will touch and overlap the neighbouring unhybridised 'p' orbital (or orbitals in the case of C_2 and C_3). The result is that the electrons in the unhybridised 'p' orbitals then become delocalised and are no longer located between their parent atoms, but instead they roam freely throughout the whole of the delocalised π system – as we saw when we were talking about Resonance.

[1] The double bonds can be only on C_1 and C_3 therefore there is no need to call it Buta-1,3-diene.



Source : Dickerson & Geis "Chemistry, Matter and the Universe"

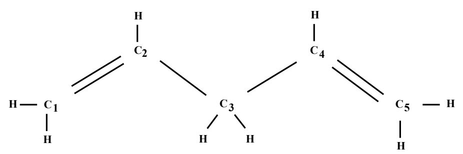
- The same phenomenon will occur in Penta–1,3–diene (also called 1,3–Pentadiene)



and in any other molecule that is composed of alternating single and double bonds.

<u>A Non-Conjugated Molecule</u>

- In contrast, Penta–1,4–diene (or 1,4–Pentadiene) will **not** be a conjugated molecule because $C_1/C_2/C_4$/and C_5 will all have both
(i) sp^2 hybridised orbitals to form their σ bonds, and
(ii) unhybridised 'p' orbitals to form their π bonds
whereas C_3 will have four sp^3 hybridised orbitals and it will have no unhybridised 'p' orbital and therefore it does not have an orbital that will overlap the unhybridised 'p' orbital of its neighbouring C atoms, and it cannot then form a "delocalised" chain with its neighbours.

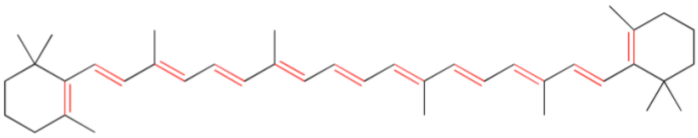


- The rules for conjugation are much more complicated than this, but that is all that you need to know of the rules for 'A' Level purposes.

Why is Conjugation important?

- The question that we need to ask now is “why is conjugation important?”, and the answer is that a) the delocalisation in conjugation imparts stability, and
b) conjugation helps to explain the perceived colour of dyes.

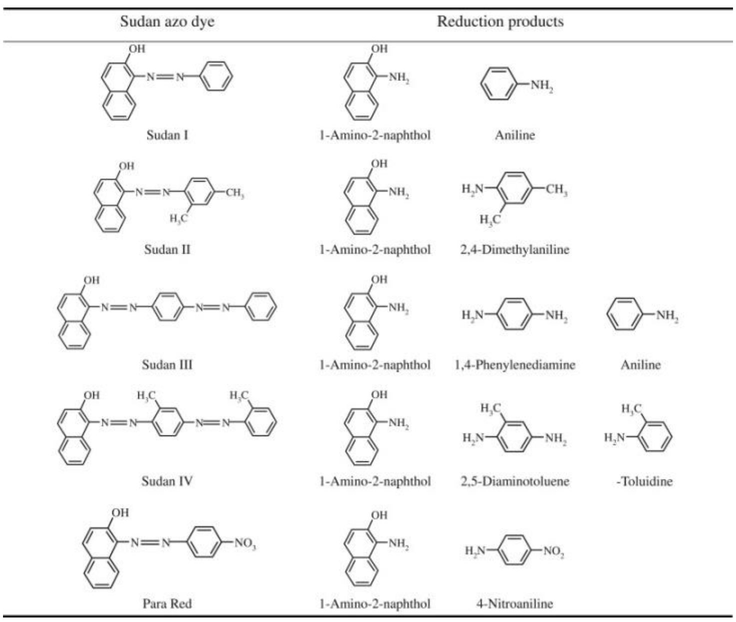
- In dyes, what is happening is that when sunlight falls on an object, then photons of light of a particular frequency are absorbed by certain conjugated organic molecules[2] and reflect the non-absorbed frequencies in the visible spectrum to the human eye – and it is these frequencies that give rise to the perceived colour of the object. For example, I know nothing about Biology, but I understand that the colour of carrots is due to the above effect in beta-carotene – and as you can see below, there is a considerable amount of conjugation in beta-carotene.



β-carotene

- If you are doing Biology as one of your ‘A’ Levels, then you may be aware that the European Union has restricted the use of certain aromatic compounds (i.e. benzene and benzene-like molecules that possess one or more delocalised π rings) because they are carcinogenic – and the diagram below shows you some of the **conjugated** molecules that are derived from a family of dyes called “Sudan” red.

- In 2005 the UK Food Standards Agency enforced the recall of 359 products that were accidentally contaminated by the dye Sudan Red (cf. http://news.bbc.co.uk/nol/shared/bsp/hi/pdfs/18_02_05_sudan.pdf)

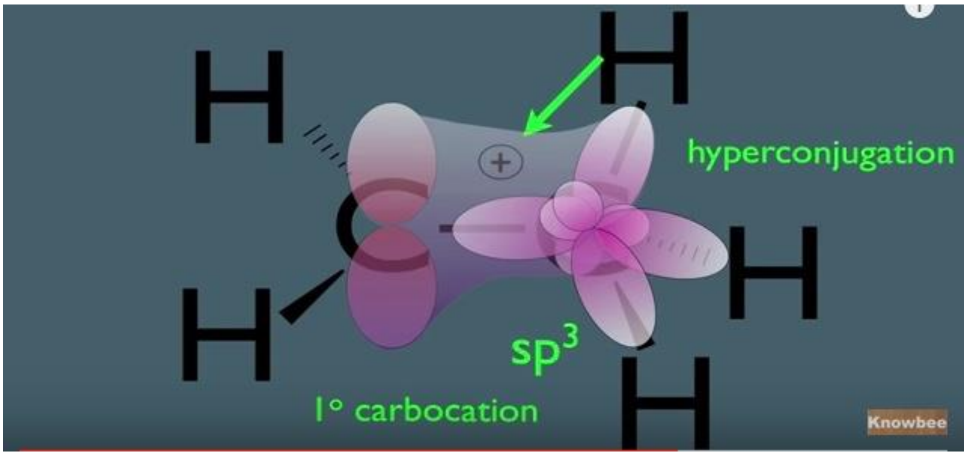


Source : sciencedirect.com

[2] When the photon of light is absorbed by the molecule, then the increase in energy causes electrons to jump from the energy level of their own normal Molecular Orbital to the energy level of a higher MO (e.g. from π to π*), but that is not something that you need to know.

Hyperconjugation

- Conjugation exists when an electron in an unhybridised ‘p’ orbital wanders or leaches into an adjoining π system via an adjoining unhybridised ‘p’ orbital in that π system if the two unhybridised ‘p’ orbitals lie in the same plane. In contrast, Hyperconjugation exists when there is *no electron* in an unhybridised ‘p’ orbital and instead it carries a positive charge. If an electron in a *hybridised* orbital which is in the same plane as the unhybridised ‘p’ orbital then wanders into/leaches into the unhybridised ‘p’ orbital which is carrying the positive charge, then hyperconjugation has taken place. The nice little video from Knowbee below shows it as the spreading of the positive charge (although technically it is the delocalisation of the electron that is causing the hyperconjugation).



Source: https://www.youtube.com/watch?v=_mEJ1aYmYo4
(“Knowbee” is a subsidiary of the US National Academy of Sciences)

- When we get to Chapter 8 you will need to know that the stability of a carbocation will increase according to the number of alkyl groups that are attached to it

the ability to donate electron density increases leftwards

Increasing Stability of the carbocation <——————————————————

3˚ alkyl	>	2˚ alkyl	>	1˚ alkyl	>	methyl
$-C(CH_3)_3$		$-CH(CH_3)_2$		$-CH_2(CH_3)$		$-CH_3$

and if you think about it, what is happening is that as more and more alkyl groups are involved, then the electrons from a larger and larger number of *hybridised* orbitals (all parallel to each other) are now being delocalised over a larger volume of space (and delocalisation confers stability).

- In the line-up on stability above I have used branched-chained alkanes in the form of 1˚/ 2˚/and 3˚ alkyl groups, but the delocalisation would also take place in an increasingly larger and larger straight-chained alkane viz.

Increasing Stability of the carbocation

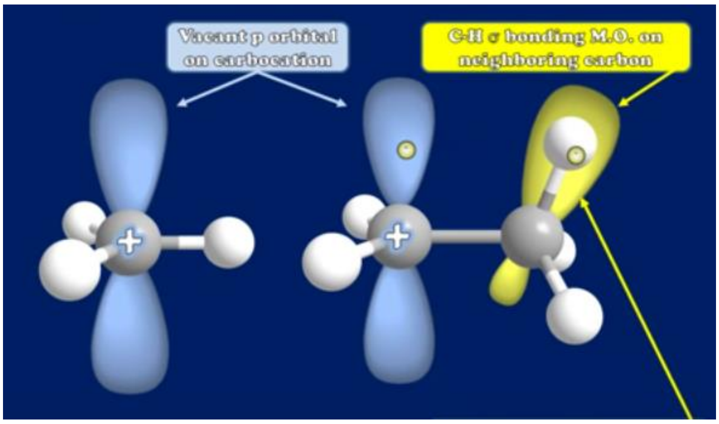
<——————————————————————

$-CH_3$ $-C_2H_5$ $-C_3H_7$ $-C_4H_9$ .... and so on

- Hyperconjugation is a construct that had to be introduced after Robert Mulliken[3] found out (in the 1930s) that increasing the number of alkyl substituents on a carbocation (or a radical centre) leads to an increase in stability. There is more to it than that, but **that is all that you need to know about Hyperconjugation for "A" Level purposes.**

- There is a good visual demonstration of how an electron 'escapes'/ 'leaches' out into a neighbouring species on ChemSurvival https://www.youtube.com/watch?v=Oa-yZGz2AdY

- A "carbo-cation" is a **positively charged Carbon species** such as CH_3^+, or $C_2H_5^+$. The species on the left below is a methyl carbo-cation CH_3^+, and the one on the right is an ethyl carbo-cation $C_2H_5^+$, and the video shows how it is that the electron from the yellow hybridised ' sp^3 ' orbital leaches into the vacant adjoining blue unhybridised 'p' orbital. *(The orbitals are of course not coloured in real life.)*



- I would not pursue Conjugation and Hyperconjugation any farther if I were you. It is **not** part of the UK 'A' Level syllabus – **although its ramifications do effect the Activation and Deactivation of Benzene rings.**

- OK, let us now start the official Second Year 'A' Level Chemistry syllabus.

[3] ... of MIT and who won his Nobel Prize in 1966.