UV-VISIBLE SPECTROSCOPY – BONDING THEORY

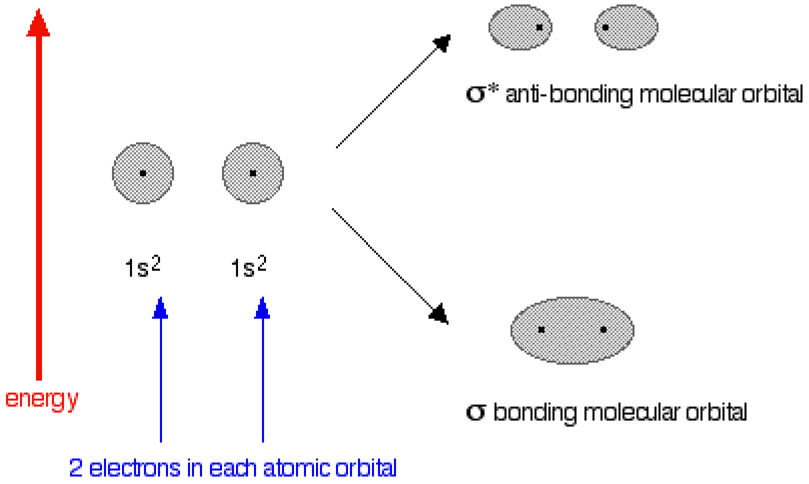
1. a) (i) Sigma bonds are formed by end-to-end overlap between atomic orbitals (actually, this is the only possibility for hydrogen atoms). The sigma orbital represents the region of space where there is a defined chance of finding the electrons. On average, they are most likely to be found on the line between the two nuclei, and the bond is due to the attractions between the two nuclei and the pair of electrons.

(ii) Molecular orbital theory demands that if you start with two atomic orbitals, you must end up with two molecular orbitals. The anti-bonding orbital has a much higher energy than the bonding orbital. Under normal circumstances, any anti-bonding orbital will be empty.

(iii) The shape of the orbital shows a zero chance of finding the electrons mid-way between the nuclei, and a much greater chance of finding them either to the left or the right of the hydrogen nuclei. That means that repulsions between the two nuclei are high, and the arrangement is energetically unstable.

(iv) This orbital is at a lower energy (is more energetically stable) than the original atomic orbitals or the anti-bonding orbital.

b)

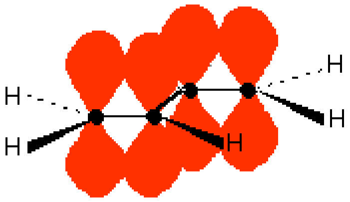


In helium you again start with two atomic orbitals and so must end up with two molecular orbitals – a bonding one and an anti-bonding one. In this case, there are four electrons, and so each of these would have to contain two electrons. But now any gain in energetic stability in the formation of the bonding orbital is offset by the loss of stability in forming the anti-bonding orbital. There is no energetic advantage in forming the He_2 molecule.

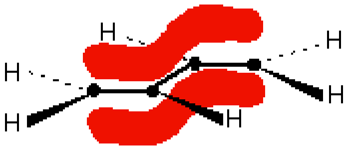
c) You would get sigma and pi bonding orbitals, and sigma and pi anti-bonding orbitals.

d) A non-bonding orbital contains a lone pair at the bonding level.

2. a) When carbon atoms form double bonds, each one uses three of its four bonding electrons to form sigma bonds by end-to-end overlap with orbitals in other elements, but one of the p electrons on each carbon isn't involved with this. In this case, the molecule can be thought of like this:



These four orbitals all overlap sideways to produce two delocalised pi bonding orbitals, each containing two electrons, and two pi anti-bonding orbitals. We normally only draw one of the bonding orbitals:

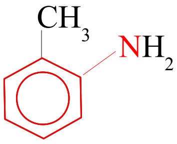


This interaction of two double bonds to produce a delocalised electron system over all four atoms is known as conjugation.

b) (i) $CH_2=CH-CH_2-CH=CH_2$ (There is no delocalisation. The double bonds are too far apart to be conjugated.)

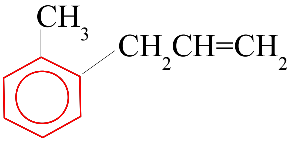
(ii) $CH_2=CH-CH=CH-CHO$ (The delocalisation extends as far as the C=O double bond in the aldehyde group.)

(iii)



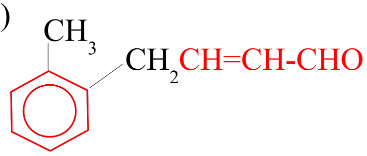
(Strictly speaking, only the nitrogen in the NH_2 groups is involved in the delocalisation, but there is inconsistency in this! As drawn here, it makes it consistent with part (vii) below, but I'm not sure whether there is a definitive view on whether you should include the whole group or not. Normally, of course, you never colour the delocalised bits separately from the rest of the molecule – you just talk about the interaction between the nitrogen lone pair and the ring electrons and ignore the hydrogens.)

(iv)



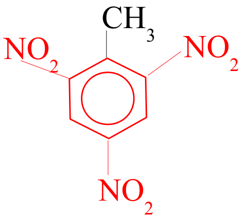
The double bond is too far from the ring to conjugate with it.

(v)

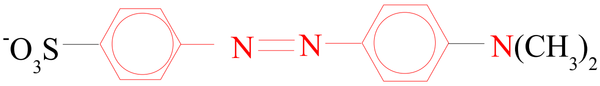


There are two regions of delocalisation, but the CH_2 group stops them interacting.

(vi)



(vii)



Remember that delocalisation doesn't extend over $-SO_3^-$ groups.

(viii)