

## 2.3: Effect of Non-bonding Electrons

### Compare the UV absorption spectrum of benzene and pyridine.

Benzene has a set of conjugated  $\pi$ -bonds and the lowest energy transition would be a  $\pi$ - $\pi^*$  transition as shown in Figure 2.3.17.

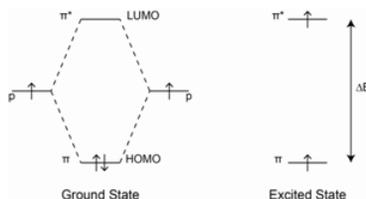


Figure 2.3.17. Representation of the lowest energy transition in benzene.

The UV/VIS absorption spectrum for benzene is shown in Figure 2.3.18

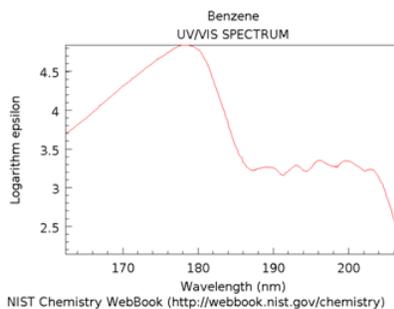


Figure 2.3.18. Ultraviolet absorption spectrum of benzene.

Benzene absorbs radiation in the vacuum ultraviolet over the range from 160-208 nm with a  $\lambda_{\max}$  value of about 178 nm. Pyridine has a similar conjugation of double bonds comparable to what occurs in benzene.

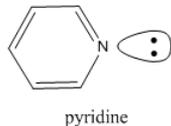


Figure 2.3.19 shows filled bonding molecular orbitals (BMOs), empty anti-bonding molecular orbitals (ABMOs) and the location of non-bonding electrons.

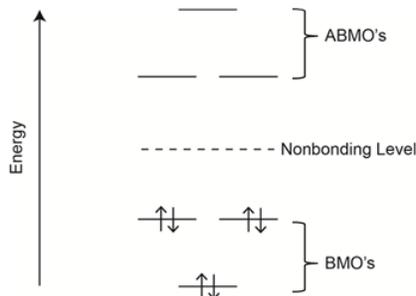


Figure 2.3.19. Representation of the relative energies of bonding molecular orbitals (BMOs), anti-bonding molecular orbitals (ABMOs) and non-bonding electrons.

For pyridine, the lowest energy transition involves the  $n$ - $\pi^*$  orbitals and this will be much lower in energy than the  $\pi$ - $\pi^*$  transition in pyridine or benzene. The UV/VIS absorption spectrum of pyridine is shown in Figure 2.3.20

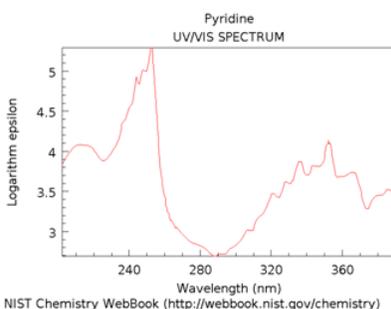


Figure 2.3.20. UV/VIS absorption spectrum of pyridine.

The shift toward higher wavelengths when compared to benzene is quite noticeable in the spectrum of pyridine, where the peaks from 320-380 nm represent the  $n-\pi^*$  transition and the peak at about 240 nm is a  $\pi-\pi^*$  transition. Note that intensity and therefore the molar absorptivity of the  $n-\pi^*$  transition is lower than that of the  $\pi-\pi^*$  transition. This is usually the case with organic compounds.

Dye molecules absorb in the visible portion of the spectrum. They absorb wavelengths complementary to the color of the dye. Most  $\pi-\pi^*$  transitions in organic molecules are in the ultraviolet portion of the spectrum unless the system is highly conjugated. Visible absorption is achieved in dye molecules by having a combination of conjugation and non-bonding electrons. Azo dyes with the  $N=N$  group are quite common, one example of which is shown in Figure 2.3.21.

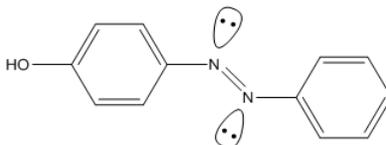


Figure 2.3.21. Structure of yellow azo dye.

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