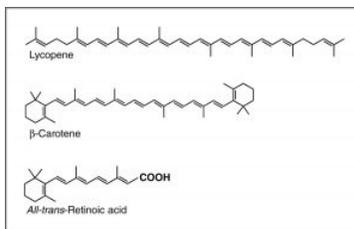
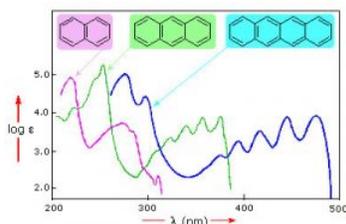


2.2: UV-Vis Spectroscopy and Chromophores - or Why are Carrots Orange?

One common recommendation from doctors is that we eat plenty of highly colored fruits and vegetables. The compounds that give these foods their strong color have a number of commonalities. For example, the compound that gives carrots and sweet potatoes their distinctive orange color is beta-carotene. You might well notice its similarity to retinal. The compound that contributes to the red color of tomatoes is lycopene. Molecules of this type are known generically as pigments.



The wavelengths at which a compound absorbs light depends on the energy gap between the orbitals that are involved in the transition. This energy gap is determined by the structure of the molecule. A molecule with only single bonds absorbs light at shorter wavelengths (in the high-energy UV), while more complex bonding patterns are associated with the absorption of visible light. For example, the presence of multiple pi bonds and their interactions within the molecule can affect the energy gap between the molecular orbitals. Recall our discussion of graphite. Rather than thinking of graphite as sheets of fused six-membered rings with alternating single and double bonds, we can think of each bond as a localized sigma bond and a delocalized pi bond. There are huge numbers of pi molecular orbitals spread over the whole sheet of carbon atoms. The more pi MO's there are, the more the energy gap between these orbital decreases; that is, the less energy (longer wavelength light) is needed to move an electron from a pi to pi* orbital. In the case of network substances like graphite and metals, the energy gap between the orbitals becomes negligible, and we think of the bonding model as a band of molecular orbitals. In these cases, many wavelengths of light can be absorbed and then re-emitted which gives graphite and metals their characteristic shininess. In substances like lycopene or β -carotene we also find this pattern of alternating single and double bonds. We say that compounds with this pattern of alternating single and double bonds (e.g. $-\text{C}=\text{C}-\text{C}=\text{C}-$) are conjugated, and we can model the bonding in the same way as graphite. There are pi MO's that can extend over the region of the molecule, and the more orbitals there are, the closer together in energy they get.

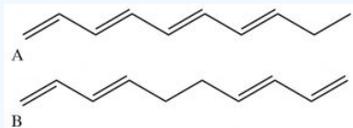


For an isolated $\text{C}=\text{C}$ double bond, the energy required to promote an electron from the pi to the pi* orbital corresponds to the light in the UV region (around 170 nm), but as the number of double-bonds that are conjugated (separated by single bonds) increases, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases. Eventually, the wavelength of light needed to promote an electron from the HOMO to the LUMO moves into the visible region, and the substance becomes colored. (Note that it does not become the color of the light that is absorbed, but rather the remaining light that is transmitted or reflected). These conjugated regions of molecules are called chromophores.^[5] The longer the conjugated section of the molecule, the longer the wavelength of light that it absorbs. You will notice that both lycopene and β -carotene contain large chromophore regions.

Samples of UV-VIS absorption spectra are shown here. Note that in contrast to the atomic absorption spectra we saw earlier (which consisted of sharp lines corresponding to the wavelength of light absorbed by atoms) these spectra are broad and ill-defined. In addition, you can see that the longer (larger) the chromophore, the longer the wavelength that is absorbed—and each of these compounds appears to be a different color. The fact that the peaks in these spectra are not sharp means that UV-VIS spectroscopy is typically not used for identification of compounds (see below for IR and NMR spectroscopy which can be used for this purpose). However, the amount of light absorbed is proportional to the concentration of the substance and therefore UV-VIS spectroscopy can be used to determine the concentration of samples.

Questions to Answer:

- Construct a representation that can help you explain why compounds with longer chromophores absorb lower energy photons than those with shorter chromophores
- Which compound do you think absorbs photons of the lowest energy light? Explain your reasoning, using a molecular orbital diagram to illustrate.



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