CH1101 CLASSNOTES 1

1. Delocalization and Conjugation:

In our daily life we see many different colours-from the greens and browns outside to the bright blues and reds of the clothes that we wear. All these colours result from the interaction of light with the dyes/pigments in these different objects. Some of the frequencies of light are absorbed, others are transmitted. All these different pigments have one thing in common—lots of double bonds. For example, the pigment responsible for the red-orange colour in carrots is β -carotene (fig. 1), a long-chain polyalkene. All the eleven double bonds in β -carotene are separated by only one single bond from each other. We would call such an arrangement of double-single-double bonds as a conjugated system. Essentially, it allows the p-orbitals to interact with each other provided the planarity is maintained.

Figure 1: The conjugated double bonds in β-carotene

We will now try to understand the special properties of conjugated π -electron systems based on molecular orbitals.

1.1 Molecular orbitals of π -conjugated systems: Hückel Theory:

The model which we would employ is known as the Hückel theory for π -conjugated systems. It is based on the following assumptions:

- 1. The sigma bonding framework in not considered; only the π -molecular orbitals are of importance.
- 2. The model is based on the confinement of electrons in a box (here the box refers to the molecule). Each molecular orbital is a one electron wavefunction. However, we will assume them to be valid for two electrons also.
- 3. The π -molecular orbitals (MOs) are built from a linear combination of atomic orbitals (AOs). The number of MOs will be equal to the number of AOs. For example, if three atomic orbitals Φ_1 , Φ_2 and Φ_3 interact with each other, we will have three MOs (according to eq. 1). Each MO has a different combination of coefficients c_1 , c_2 , and c_3 . In simple terms,

the coefficients represent the contribution of each atomic orbital to a particular molecular orbital.

Equation 1:

$$\psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3$$

1.2 Molecular Orbitals of Butadiene:

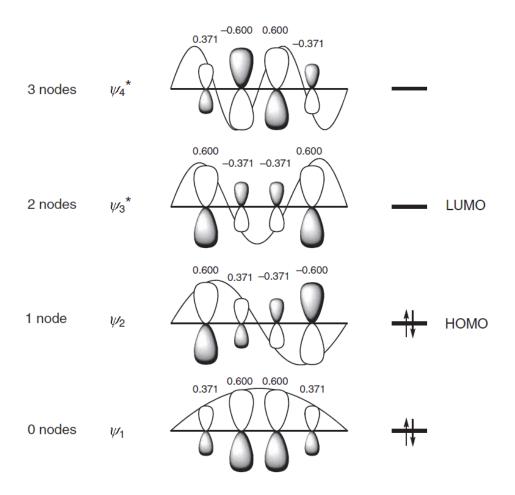


Figure 2: π -molecular orbitals of butadiene

In fig. 2, the four π -molecular orbitals of butadiene are shown. Note that the lowest MO does not have any node while the next three MOs have 1, 2 and 3 nodes, respectively. The four π -electrons are filled in the lowermost two orbitals. The highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) are also shown in fig. 2.

Now we will consider three molecules: ethylene, butadiene and hexatriene. While ethylene has a single C=C bond, butadiene and hexatriene have 2 and 3 double bonds in conjugation, respectively. We are interested to know what happens to the

relative energy of the π -MOs when we move from ethylene to hexatriene. A comparison is shown in the diagram in fig. 3. As shown, hexatriene has the smallest HOMO-LUMO energy gap among ethylene, butadiene and hexatriene. In fact, this is a general trend in going to longer conjugated systems. This has important implications in their spectroscopic properties. Due to a lower HOMO-LUMO energy gap, hexatriene absorbs at higher wavelengths than ethylene and butadiene.

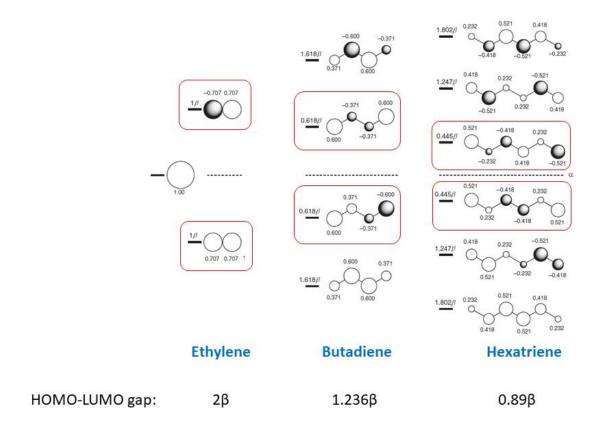


Figure 3: The energies and coefficients of the π -molecular orbitals of conjugated systems. The HOMO and LUMO of ethylene, butadiene and hexatriene are marked as red boxes. It can be noted that in going from ethylene to hexatriene, the HOMO-LUMO gap decreases.

1.3 Conjugation and Colour:

The trend in the decrease of the HOMO-LUMO gap with increasing conjugation length would help us to explain the colour of β -carotene. As shown in fig. 4, human eyes can detect only a small region of the complete electromagnetic spectrum. This region from 400-700 nm is called the visible range.

As the energy difference between the HOMO and LUMO for butadiene is less than that for ethylene, we would expect butadiene to absorb light of longer wavelength than ethylene (the longer the wavelength, the lower the energy, $\Delta E = hc/\lambda$). This is found to be the case: butadiene absorbs at 215 nm compared to 185 nm for ethylene. In general, the more conjugated a compound is, the smaller the energy transition between its HOMO and LUMO and hence the longer the wavelength of light it can absorb. Hence, UV–visible spectroscopy can tell us about the conjugation present in a molecule.

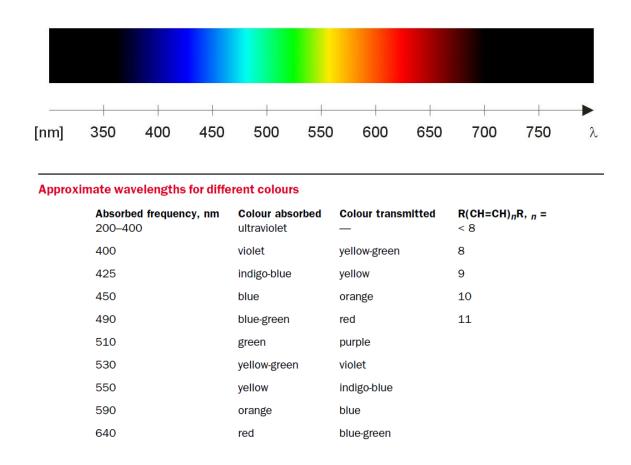


Figure 4: The visible spectral region (above) and the approximate wavelengths for different colours, their complementary colours and the variation in colour in the conjugated systems.

Both ethylene and butadiene absorb in the far-UV region of the electromagnetic spectrum (215 nm is just creeping into the UV region). However, if we extend the conjugation further, the gap between HOMO and LUMO will eventually be sufficiently reduced to allow the compound to absorb visible light and hence be coloured. As can be seen from fig. 4, once the number of conjugated double bonds is 8 or more, the

compounds start absorbing in the visible range. For example, β -carotene absorbs in the blue-green range and hence the transmitted colour that we see is red.

2. Formal charges in Lewis dot structures and actual charge density in molecules:

In organic chemistry while drawing mechanisms, very regularly we use the curly arrows to show the movement of electrons from an environment of high negative charge density to one of lower negative charge density. But sometimes if we follow only the interaction between the charges, we would land into problems. Let's look at the three reactions (R1, R2 and R3) shown in fig. 5. In case of R1, there is no ambiguity. A hydroxide ion indeed attacks the central carbon atom of the trityl cation. Hence, in this example the reaction outcome can be predicted by moving the negative charge from hydroxide to the

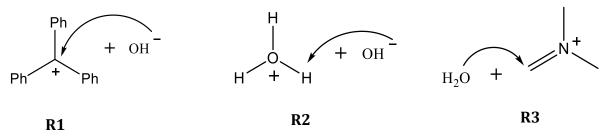


Figure 5: Reactions involving charged reactants

carbon atom possessing a formal positive charge. However, the outcome of the reactions R2 and R3 can't be predicted based on arrow pushing involving only charges. The hydroxide ion never attacks the oxygen atom in hydronium atom which apparently has a positive formal charge of +1. Similarly, water will never attack the nitrogen in the iminium ion in R3. Therefore, the reactions R2 and R3 suggest that there is a problem in following formal charges as often shown in Lewis structures. Of course, you all know now that such outcomes can be explained based on the M0 interactions.

Now let's have a look at the calculated charge distributions in trimethylamine and tetramethyl ammonium cation (fig. 6). There is nothing unusual about the charge distribution in trimethylamine. Nitrogen being the more electronegative element, contains a partial negative charge of -0.56 which is cancelled by the fractional +0.19 charge on each of the three methyl groups thus making the molecule on a whole neutral. But if we look at the calculated charge density in tetramethylammonium cation, we find something very interesting. According to the formal charge in Lewis dot structure, we expect a unit positive charge on nitrogen. However, the results show that the situation is

quite different. Even in this positively charged ammonium cation, the more electronegative nitrogen still holds a partial negative charge of -0.36 while each of the three methyl groups carries a partial positive charge of +0.34. Logically speaking, it is not surprising at all. Nitrogen being more electronegative than carbon, will always have a negative charge on it, irrespective of the net charge on the molecule.

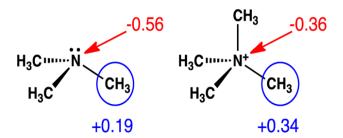


Figure 6: Calculated charge distribution in trimethylamine and tetramethylammonium salt (**ref**: D. A. Dougherty, *Acc. Chem. Res.* **2013**, *46*, 885).

3. Molecular Orbital Theory and Organic Reactions:

It is possible to understand why molecules react in a particular way by looking at the orbitals involved. The key ideas which grow out of the orbital description provide a framework for rationalizing a great deal about chemical reactivity. During a chemical reaction, bonds are broken and new bonds are made as the reactants are transformed into the products. As a result, the electrons are redistributed during the reaction. In other words, the shapes and energies of the orbitals involved must change during the course of a reaction.

When two molecules approach each other taking part in a reaction through a collision, the following forces operate:

- 1. The occupied orbitals of one repel the occupied orbitals of the other.
- 2. Any positive charge on one attracts any negative charge on the other (and repels any positive).
- 3. The occupied orbitals (especially the HOMOs) of each interact with the unoccupied orbitals (especially the LUMOs) of the other.

The contribution of steric factors, molecular orbitals and charge interactions toward the interaction energy between two molecules (e.g. a nucleophile and an electrophile), when they approach each other leading to the transition state is combined in equation 2. The middle term is related to the interaction of molecular orbitals.

Equation 2:

ΔE (interaction energy): Σ sterics – Σ orbital overlap/(E_{LUMO} – E_{HOMO}) + Σ charge interaction Reactivity

(Interaction between frontier molecular orbitals)

HOMO-LUMO Interactions Dictate Chemistry:

During the course of a reaction, all of the orbitals change to some extent. However, the most significant changes, particularly in the early stages of a reaction, can be thought of as arising from an interaction between the highest occupied MO (HOMO) of one reactant and the lowest unoccupied MO (LUMO) of the other. This HOMO-LUMO interaction essentially lowers the energy of some electrons and this can be identified as the driving force for a reaction. The outcome of different types of orbital interactions, is shown in fig. 5 for two reactants A and B.

When A and B approach each other leading to a collision, there are two pairs of HOMO-LUMO interactions (as shown by green lines in fig. 7). However, according to eq. 2, it can be understood that the interaction between the HOMO-LUMO pair in which the energy gap is smaller would play the major role in the reaction.

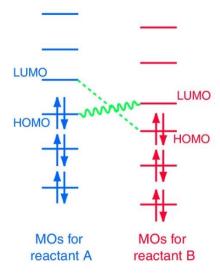


Figure 7: HOMO-LUMO interactions during a reaction between two reactants A and B.

In general, in most of the organic reactions, we will consider the following MO interactions during a reaction: HOMO (Nucleophile/base) and LUMO (Electrophile/acid). One can follow these guidelines to decide the MOs:

- 1. First decide the nucleophilic and electrophilic partners in a reaction.
- 2. Once that is decided, look at the HOMO of the nucleophile and the LUMO of the electrophile.
- 3. The coefficients in the MOs will tell you which atom(s) are involved in such interactions (donating or accepting electrons).

There are various kinds of MOs present in molecules. A rough ordering of their energy levels is shown below.

$$\sigma^* \ antibonding \\ \pi^* \ antibonding \\ Energy \qquad Nonbonding \ orbitals \ (including \ lone \ pairs) \\ \pi \ bonding \\ \sigma \ bonding$$

4. Hyperconjugation/ σ -Conjugation:

Carbocations are important intermediates in a variety of organic reactions. The stability order of the carbocations follows the sequence shown in fig. 8. Tertiary carbocations possess higher stability than secondary, primary and methyl carbocations.

Figure 8: The stability order among various types of carbocations

The higher stability of tertiary carbocations can be attributed to the +I effect of three -CH $_3$ groups. However, it has be found that other than the inductive effect, the alkyl groups also release electrons through another effect called hyperconjugation or σ -conjugation. In this case, the C-H σ -bond of the neighbouring carbon interacts with the

empty p-orbital of the carbocation. This brings extra stabilization as the two σ -electrons in the C-H bond become lower in energy as shown in fig. 9. σ -conjugation is also used to explain the higher stability of substituted alkenes.

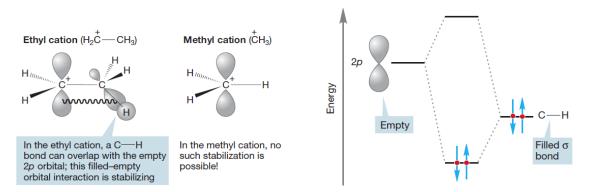


Figure 9: The presence and absence of σ -conjugation in the ethyl and methyl carbocations. The stabilization of the σ -electrons of the C-H bond is also shown.