### Bond and Energy Characteristics of Conjugated System



Hydrogenation of alkenes releases energy. If you measure the heat released from hydrogenation of the above compounds, the conjugated compound releases 15 kJ/mol less (was at a lower energy to begin with).



Recall how we can show the energy levels of the atomic orbitals of C. If the C is  $sp^2$  hybridized, two of the 2p orbitals "combine" with the 2s orbital to form two  $sp^2$  hybrid orbitals.



The following molecular orbital (MO) diagram shows the construction of molecular orbitals from the hybrid orbitals of two sp<sup>2</sup> hybridized carbons doubly bonded together (i.e., ethane). One electron pair in the  $\sigma$  MO represents the single bond between the two

carbons (and the other two represent C-H bonds), while the electron pair in the  $\pi$  MO represents the double bond (i.e., the  $\pi$  bond) between the two carbons.





sp<sup>2</sup> Carbon Atomic Orbitals

In butadiene, all four-carbon atoms have a 2p orbital. These four **atomic** 2p orbitals will combine to produce four  $\pi$  **molecular** orbitals (the number of atomic orbitals combined equals the number of molecular orbitals formed). Since there are two double bonds, there are two bonding ( $\pi$ ) and two antibonding ( $\pi^*$ ) molecular orbitals (recall each  $\pi$  bond system is made by combining two 2p atomic orbitals).



HOMO = Highest Occupied Molecular Orbital LUMO = Lowest Unoccupied Molecular Orbital

Two double bonds means that there are  $4 \pi$  electrons in the conjugated system (1 double bond has  $2 \pi$  electrons). We can fill the 4 **molecular** orbitals with these electrons starting from the lowest energy level.



Molecules absorb energy at the specific wavelength corresponding to the  $\Delta E$  between the HOMO and LUMO. This is the basis for colour (absorption of light with a wavelength corresponding to visible light) and photosynthesis.



As the molecule becomes more conjugated, the energy gap ( $\Delta E$ ) between the HOMO and LUMO become smaller.

Molecules with  $\geq$  7 conjugated double bonds absorb light between 4000 – 8000 Å (400-800nm) and are visible to us, such as the compound shown below.

In this molecule, there are 7 bonding and 7 anti-bonding  $\pi$  MO. The energy gap between LUMO and HOMO is very small and is equal to the energy of blue light (~400 nm).

Since  $E = hc/\lambda$ , the wavelength at which this molecule absorbs is long. It absorbs blue light and we see it as yellow.



### **UV** Absorption



Woodward rules: Predicts wavelength of absorption The presence of highly conjugated compounds can be measured by using a uv spectrometer

## Absorption and Reflection of Visual Light

Absorbed Wavelength (Å)	Colour Absorbed	Visual Colour
4000-4350	violet – blue	yellow – green
4900-5000	blue- green	red
5800-5950	yellow	blue
5950-6050	orange – red	green
6050-7500	r e d	blue – green

## **Conjugated Dienes and Colour**

Beta-carotene (depicted below) is responsible for the orange-red colour in carrots. Plants produce  $10^9$  metric tons of beta-carotene per year. Carotenoids protect plants against photodamage.



*β*-carotene

# Xanthophylls

Xanthophylls are oxygenated carotene molecules. Zeaxanthin, shown below is purple.



# Zeaxanthin (purple)

In the below example astaxanthin, a blue-green pigment in algae, is converted to astascene with the addition of heat, water and oxygen. Astascene is red in colour and contains an enol functional group. Crustaceans (e.g. lobsters) eat algae in their natural habitat and thereby ingest astaxanthin. When a lobster is cooked it turns a bright red colour, which is mainly due to the formation of astascene.



Chlorophyll A (green colour in plants) is another example of a conjugated molecule that absorbs light and is essential for photosynthesis:



Heme of hemoglobin (red colour in blood) is responsible for the binding and transport of oxygen in the body:



# The Chemistry of Vision

Not all conjugated molecules are coloured (need at least 7 conjugated double bonds). They also make up the light sensitive substances responsible for the visual systems of organisms. A key component of our vision arises from the body's ability to synthesize Vitamin A from beta-carotene (shown below) in which the  $C_{40}$  beta-carotene is broken down into the  $C_{20}$  vitamin A.



In the liver vitamin A (retinol) is further oxidized to the aldehyde (retinal).



In the eye retinal reacts with a protein called opsin to give rhodopsin, the visual pigment that is the actual light sensitive substance.



Light causes the C11-C12 bond to isomerize from cis to trans. This causes a change in the 3D conformation of the protein that results in nerve impulses being sent to the brain  $\rightarrow$  vision.

Oxidation of the aldehyde to a carboxylic acid in retinal yields retinoic acid, a chemical messenger in the body that provides signals for fetal development.



Conversion of the C13 double bond in retinoic acid to the cis conformation gives the drug Accutane, which is an anti-acne drug. Isomerization is possible due to unpaired electrons in excited state. It has teratogenic properties (i.e. can cause malformations and other birth defects).



Accutane

## **Aromatic Compounds**

#### Benzene

Benzene was first isolated in 1825 by Michael Faraday. The structure was solved by Josef Loschmidt and August Kekule. The name came from benzoic acid, which had been isolated from gum benzoin.



There are many different representations of benzene:



You should know what a phenyl group is  $(C_6H_5 - different from phenol)$ 



Phenyl group

### Aromaticity

Equivalent resonance forms gives stability to a compound.

Aromatic compounds are especially stable. For benzene, the delocalization energy (stability) is 36 kcal/mol relative to that expected for cyclohexatriene.



1,2-dibromobenzene

The central circle can be used to represent the resonance within the aromatic ring. The number of conjugated pi electrons plays a key role for **stability**.

Cyclobutadiene has four pi electrons (compared to the six pi electrons in benzene), and is **very** unstable.



cyclobutadiene

To be **aromatic** (have aromaticity) a compound or ion must:

- 1. Be cyclic and conjugated around the ring
- 2. Be planar.
- 3. Have  $4n+2\pi$  electrons, where n = 0, 1, 2, 3, etc.

**Benzene** fulfills all of the above criteria. It is conjugated (has three pairs of alternating double and single bonds), it is cyclic and planar, and it has  $6 \pi$  electrons (where n = 1).

Cyclobutadiene is not aromatic. It has 4  $\pi$  electrons and doesn't fit the  $4n+2\pi$  rule.