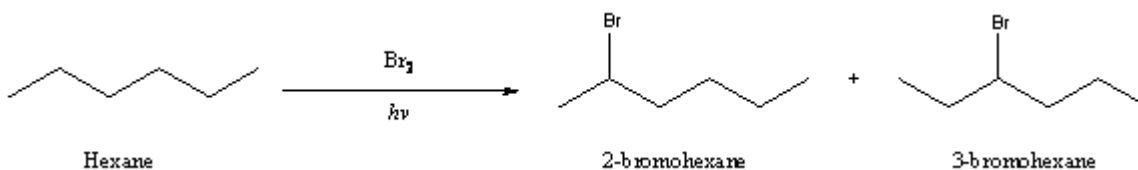**Brief Review for Chem 161 or Chem 261 on Addition and Substitution**
Reaction of an alkane with bromine to form an alkyl halide is a radical **substitution** reaction.

Hexane   2-bromohexane   3-bromohexane

Demonstration: the solvent hexane has a clear color. When a solution of bromine was added, you noticed the orange color of bromine in the hexane solution. The flask eventually went clear. (This indicates bromine has reacted with hexane to give both 2-bromohexane and 3-bromohexane and HBr as products. If bromine has not reacted, the orange color would have remained in the hexane).

Reaction of an alkene with bromine is an **addition** reaction.
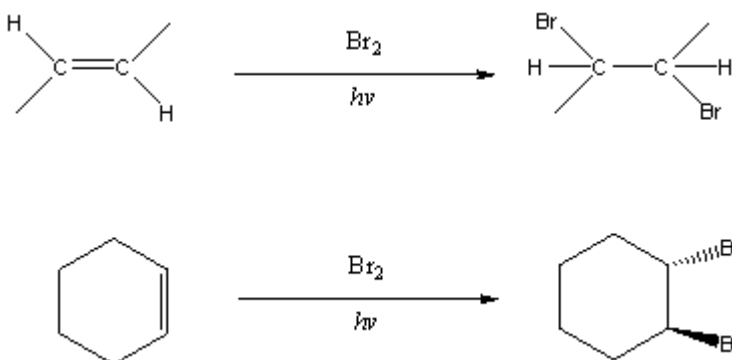
Demonstration: the cyclohexene solution is clear. When the bromine was added, the solution went clear immediately. The orange color of bromine did not sustain itself very long. (This indicates the addition reaction of alkene occurs fast and it is quicker than the substitution reaction of alkane above since the orange color of bromine disappeared right away)

Reaction of an alkyne with chlorine (or bromine) is also an *addition* reaction.

Calcium Carbide   Acetylene
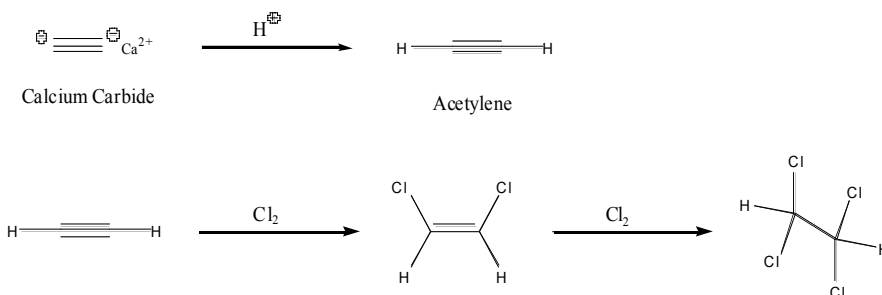
Demonstration: calcium carbide was added to dilute sulfuric acid in a graduated cylinder and generates acetylene gas. Bleach (NaOCl) was added into the cylinder and forms chlorine gas. The Cl_2 (g) generated then reacts with acetylene gas exothermically. A flame or explosion within the graduated cylinder was expected (unfortunately, we did not get the chance to watch this in class).

The acetylene reacts with chlorine gas to form 1,2-dichloroethene. The newly formed alkene can undergo subsequent addition on the double bond with chlorine gas to form saturated tetrachloroethane.

Continued from the last lecture- Addition Reaction of HBr to 1,3-Butadiene

Why does the change in temperature affect the % yield of the addition reaction?
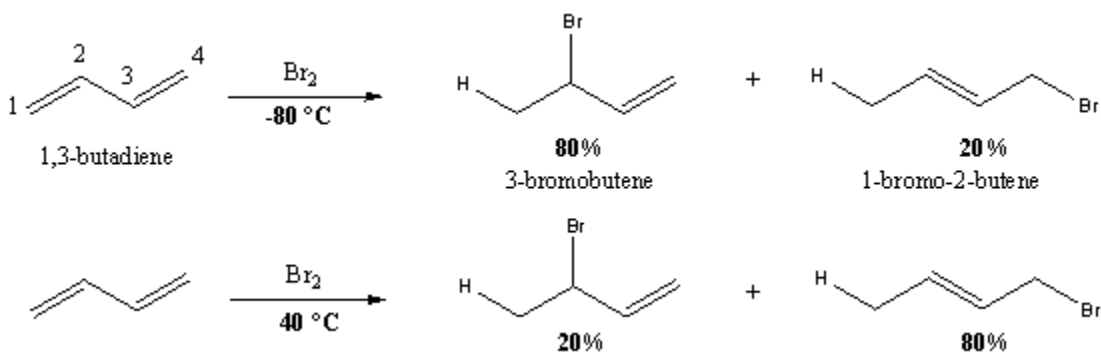
The product 3-bromobutene is an **1,2-additon** product, whereas 1-bromo-2-butene is the product of an **1,4-addition** reaction. The numbers (**1,2-** or **1,4-**) indicate the position where the H and Br added to the 1,3-butadiene. 3-Bromobutene had hydrogen and bromine atom added to C**1** and C**2** of 1,3-butadiene (hence **1,2**-addition), whereas in 1-bromo-2-butene, the hydrogen and bromine atoms are added to C**1** and C**4** of 1,3-butadiene (therefore it is an **1,4**-addition).

Mechanism of the addition reaction:
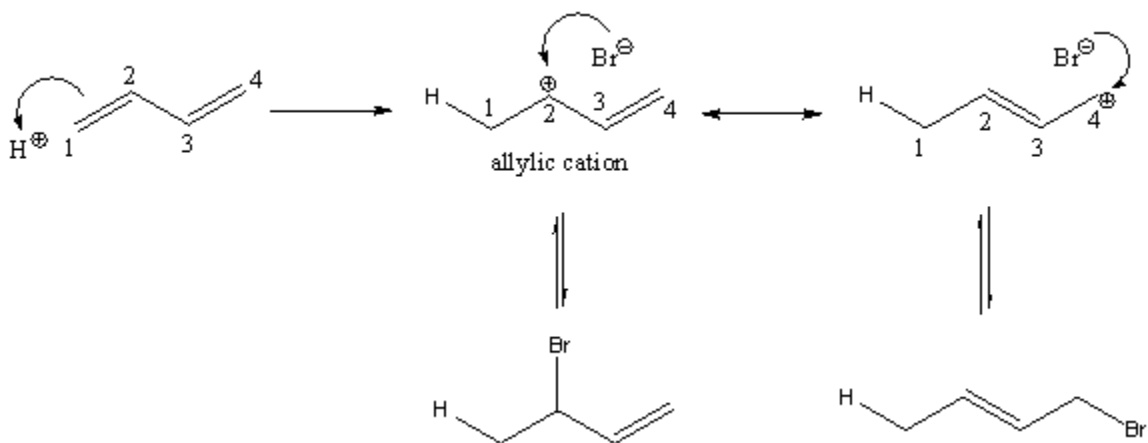
From the 2 resonance forms (connected by the double-sided arrow) of the allylic cation shown in the above figure, we see that the positive charge is shared between the two carbons (C2 and C4) with each carrying a portion of the positive charge.

Note: the allylic cation has two electrons delocalized across the three carbons. It was drawn to have two resonance forms, but it is a ***single entity***, therefore we cannot differentiate and speak of one form being a primary carbocation (therefore less stable) and the other being a secondary carbocation (therefore more stable).

***Answer to the above question*:**
- 3-brombutene has higher yield at the lower temperature because it is kinetically more favored. It formed faster than 1-bromo-2-butene. **Kinetic Control**
- 3-bromobutene has lower yield than 1-bromo-2-butene at higher temperature due to **thermodynamic control**. The addition of bromine to the allylic cation is reversible at high temperature. 3-Bromobutene can be converted back to the allylic cation and then form 1-bromo-2-butene, which is the thermodynamically more favored product.

To understand thermodynamic and kinetic control (or what I just said above), let's begin by looking at the energy diagram of a reaction.
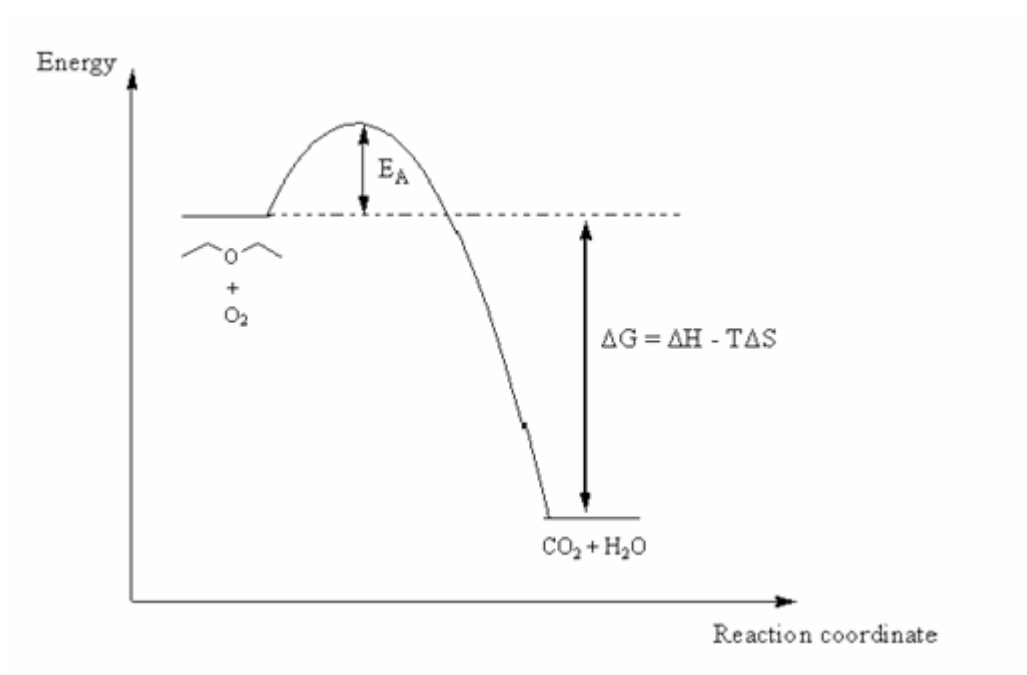
ΔG = free energy of the reaction – this determines ratio of starting material and product
ΔH = enthalpy of the reaction
T = temperature in (degrees) Kelvin
ΔS = entropy
E_A = activation energy (the amount of energy needed for reaction to proceed). This is a factor that determines the rate of a reaction.

For an exothermic reaction, there is release of heat and ΔG is always negative (depicted in the energy diagram, the starting material would be higher on the energy diagram than the product). However, the reaction is not spontaneous, and need to overcome activation energy barrier in order to form the product. Therefore, as demonstrated in lecture and in this example, we had to light ether on fire with a match which produces the initial energy for reaction to proceed.

Now let's look at the energy diagram of our butadiene and HBr addition reaction
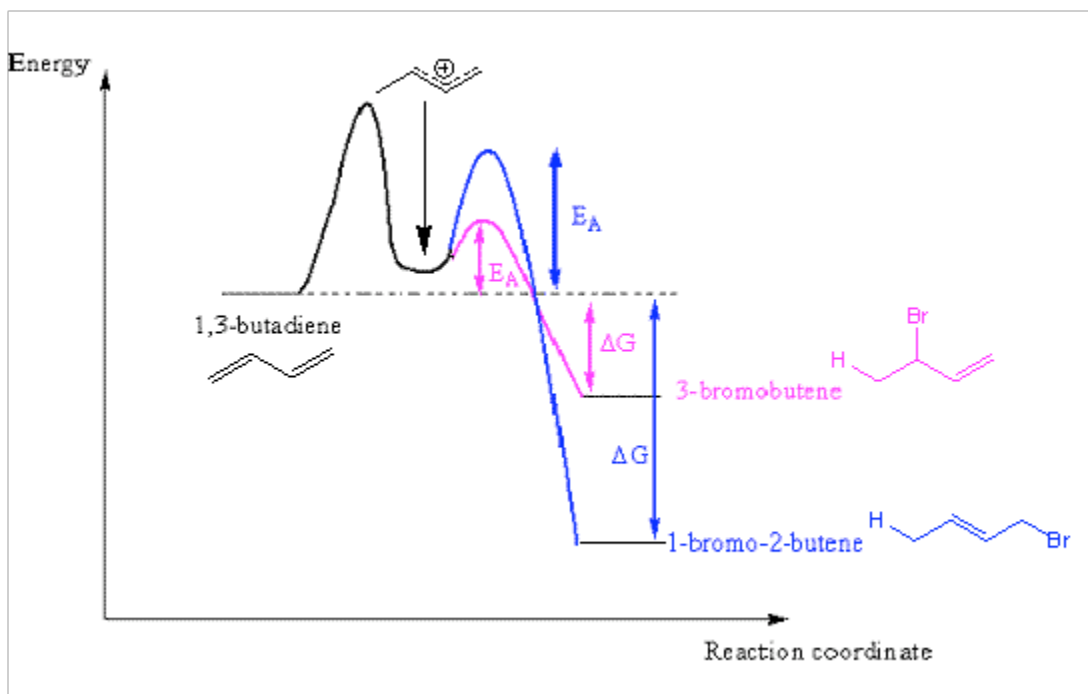
One thing to point out in the energy diagram is that the activation energy barrier to form the 1,2-product 3-bromobutene is much *smaller* than the 1,4-product 1-bromo-2-butene (so that it can be formed easier and **faster**. We call this **kinetically** favored). However, the energy of 1-bromo-2-butene is lower than 3-bromobutene, so that it is more **stable** than 3-bromobutene (we call it the **thermodynamically** favored product).
(Why is 1-bromo-2-butene more stable? This could be explained as follows: the bromine atom is bulky. It likes to stay away from the rest of the molecule to avoid steric clashes.)

At low temperature, the lower activation energy pathway (colored pink in diagram) dominates and the reaction proceeds to form 3-bromobutene. There is not enough energy for most molecules to overcome the E_A barrier to form 1-bromo-2-butene. At high temperature, there is large amount of energy available to overcome the E_A barrier forming 1-bromo-2-butene (colored in blue). Since the bromine addition to the allylic cation is reversible, 3-bromobutene can be reversed back to the allylic cation which then reform 1-bromo-2-butene. This is why the yield of 1-bromo-3-butene is high at high temperature (This is also explained in your textbook pp.606-607).

Practical application of addition reactions of conjugated systems

Example: Polystyrene Synthesis

Styrene (shown below) is a hydrocarbon molecule (contains only C and H atoms) that has a double bond conjugated with a benzene ring. A benzene ring is aromatic, and especially stable and it is less reactive than the alkene in the chain. We will see why in the next lecture.


Styrene   benzylic cation
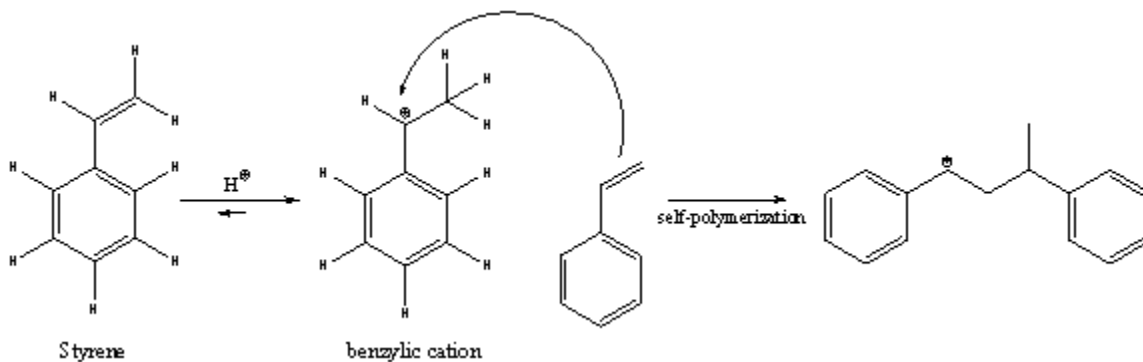
When styrene is allowed to react with an acid (e.g. sulfuric acid), the protonation occurs to give the most substituted and conjugated carbocation. In this case, the carbocation formed is called a benzylic cation (the carbon directly attached to a benzene ring is called benzylic center). The benzylic cation can react with the starting compound styrene and form another benzylic cation. If this reaction continues, it leads to eventual formation of polystyrene shown below (i.e. Styrofoam).

polystyrene   conventional abbreviation
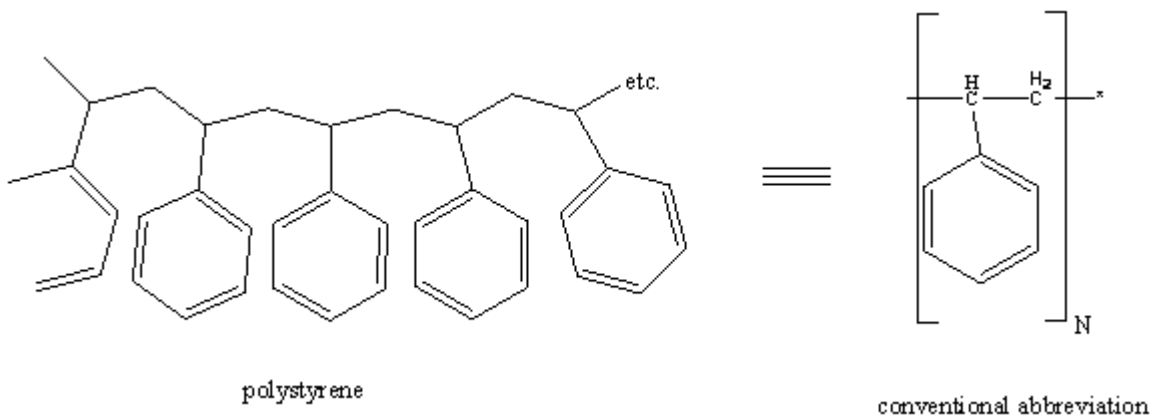
If you add heat, the reaction can be reversed to give styrene, which explains the hydrocarbon flavor in your HOT coffee.

Another Example: A reaction with styrene, 1,3-butadiene and acid

SBR
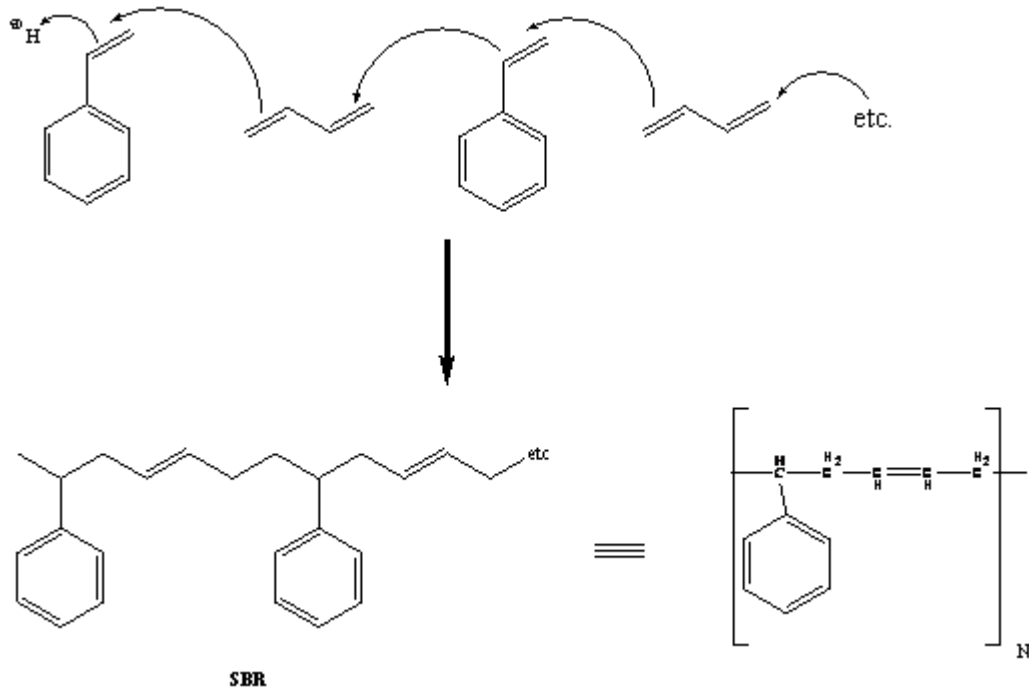
Similar to styrene polymerization, styrene and 1,3-butadiene can undergo polymerization cascade as well. The product of this polymerization is called styrene butadiene rubber (SBR). This is used in the manufacturing of tires.

Example: Rubber

Rubber is a natural product produced by rubber tree *Hivea brasiliensis*. The rubber is collected in the form of syrup (latex) and aftyer concentration as raw rubber very sticky (like chewing gum). This is not very useful.
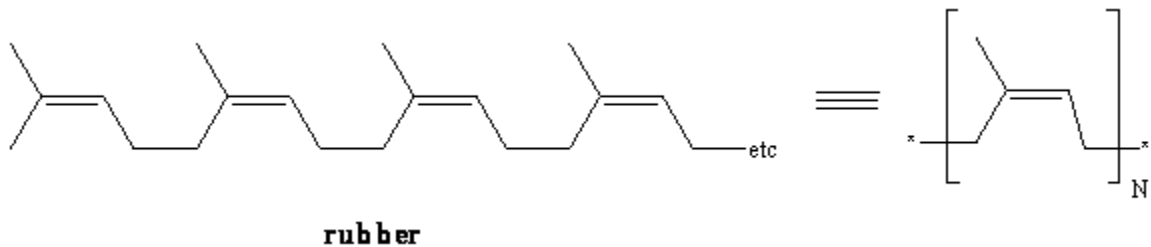
rubber

Charles Goodyear found that by adding sulfur and coal to rubber in presence of heat, sulfur cross-linked rubber or vulcanized rubber is formed. This rubber is not sticky or plastic, but rather is elastic (like a rubber band). Such forms of rubber are widely used.

Rubber can be viewed as a polymer of monomer units 2-methyl-1,3-butadiene, which is also known as isoprene.
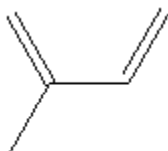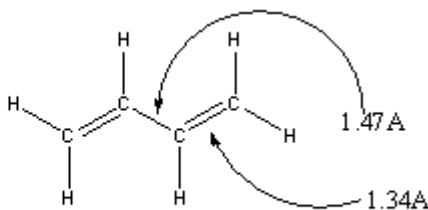

isoprene

However, rubber cannot be synthesized using the same reaction as styrene polymer. **Why?** Because the geometry of the double bond is *cis* in rubber, whereas *trans* is usually the more stable configuration. The double bond formed when reacting isoprene with acid would be in *trans* geometry

Energy Characteristics of Conjugated System
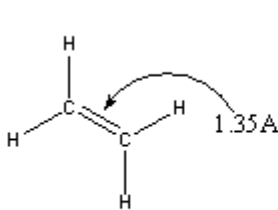

ethene   butadiene

The bond length between the double bond carbons in ethylene is ca. 1.35 Å. In 1,3-butadiene, the bond length between the double bond carbons is 1.34 Å, and the bond length between the two center single bond carbons is 1.47 Å. Compared to a normal C-C bond length of 1.54 Å, the center single bond in 1,3-butadiene is shorter (has double bond characteristic) and therefore stronger than a normal single bond.

For a conjugated system, the molecule likes to be planar because of **π molecular orbitals** that align to overlap.

Example:

In butadiene, the 4 carbon atoms each has a *2p* orbital. These atomic *2p* orbitals will overlap to produce 4 π molecular orbitals (the number of atomic orbitals combined should give the same number of molecular orbitals). Since there are two double bonds, there would be two bonding and two antibonding π molecular orbital (recall each π bond is made by combining two *2p* atomic orbitals. It has a bonding and anti-bonding molecular orbital). As well two double bonds means there are 4 π electrons in the

conjugated system (1 double bond has 2 π electrons), we can fill the 4 molecular orbitals with these electrons starting from the lowest energy level.
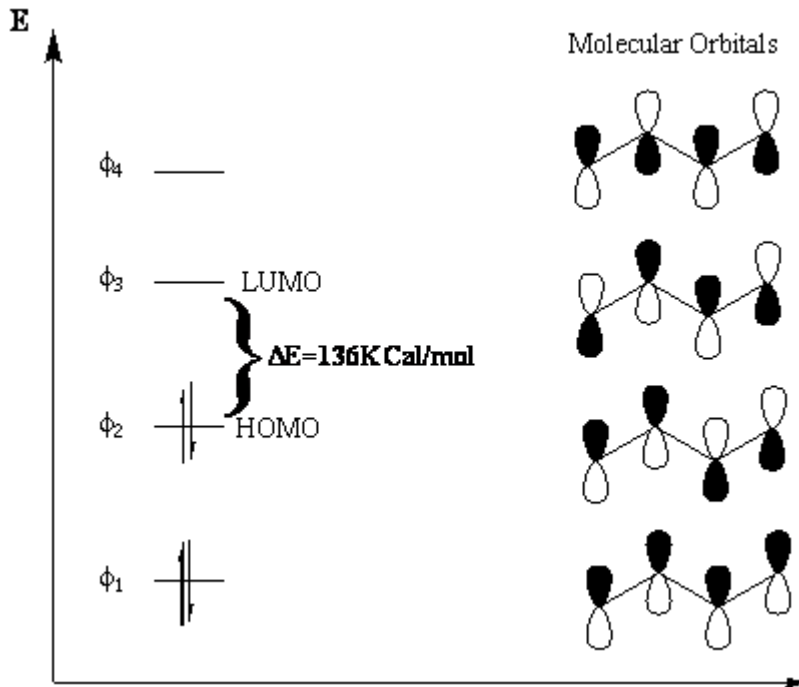
HOMO stands for Highest Occupied Molecular Orbital
LUMO stands for Lowest Unoccupied Molecular Orbital

Molecules that are conjugated absorb energy at the specific wavelength. This is also the basis for color and photosynthesis.
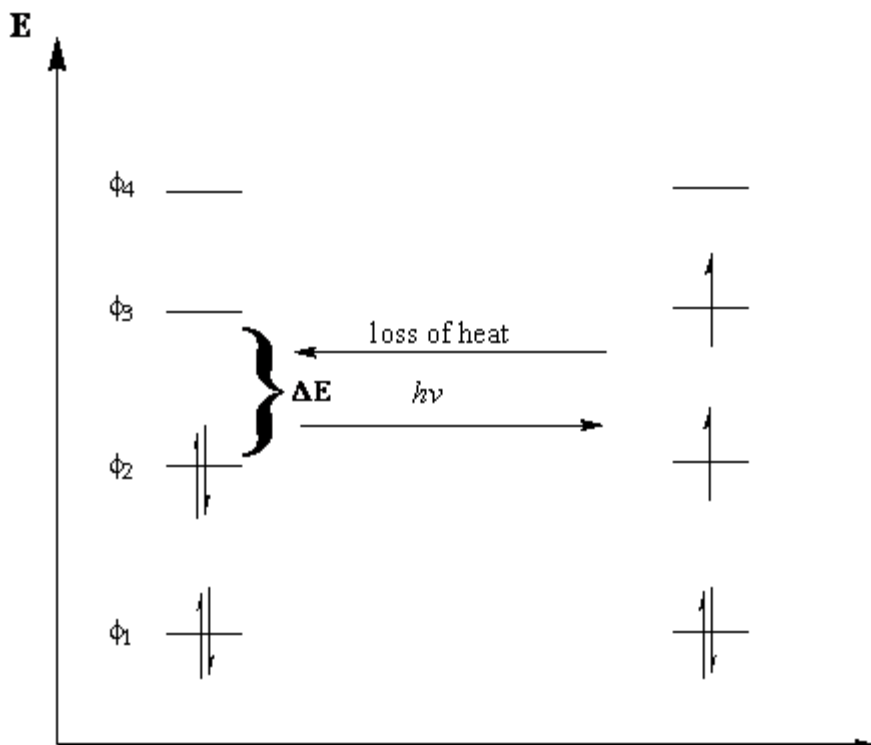
As the molecule become more conjugated, the energy gap (ΔE) between HOMO and LUMO become smaller.

A molecule with ≥ 7 conjugated double bonds absorbs light between $4000 - 8000$ Å in the visible region such as the compound shown below.

In this molecule, there are 7 bonding and 7 anti-bonding π molecular orbital. The energy gap between LUMO and HOMO is very small. Since $E = hc/\lambda$, the wavelength at which this molecule absorbs would be long. It absorbs blue-violet and we see it as yellow.

E

ϕ_{14} —————

ϕ_{13} —————

ϕ_{12} —————

ϕ_{11} —————

ϕ_{10} —————

ϕ_{9} —————

ϕ_{8} ————— LUMO

$\left.\vphantom{\begin{matrix}a\\b\end{matrix}}\right\}$ **ΔE**

ϕ_{7} —⇅— HOMO

ϕ_{6} —⇅—

ϕ_{5} —⇅—

ϕ_{4} —⇅—

ϕ_{3} —⇅—

ϕ_{2} —⇅—

ϕ_{1} —⇅—