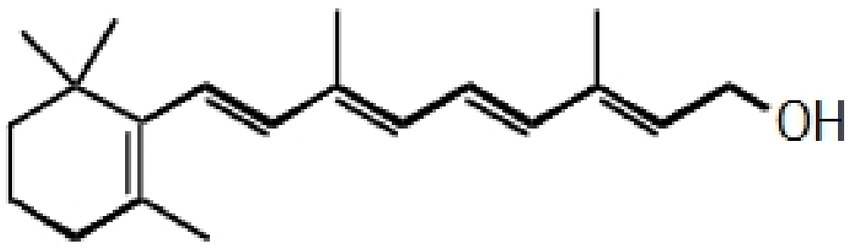
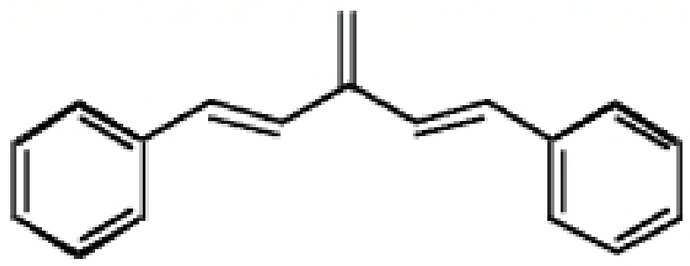
Conjugation.

Conjugation relies on the partial overlap of p-orbitals on adjacent double or triple bonds. One of the simplest conjugated molecules is 1,3-butadiene.

Conjugation comes in three "flavors," the simplest of which is the normal straight-through (linear) conjugation seen in many biomolecules (such as Vitamin A).



However, it is possible for two systems to be in "cross-conjugation" with each other, as in the example below (the two benzene rings are cross-conjugated, NOT conjugated!):



Conjugation is broken completely by the introduction of saturated (sp^3) carbon:

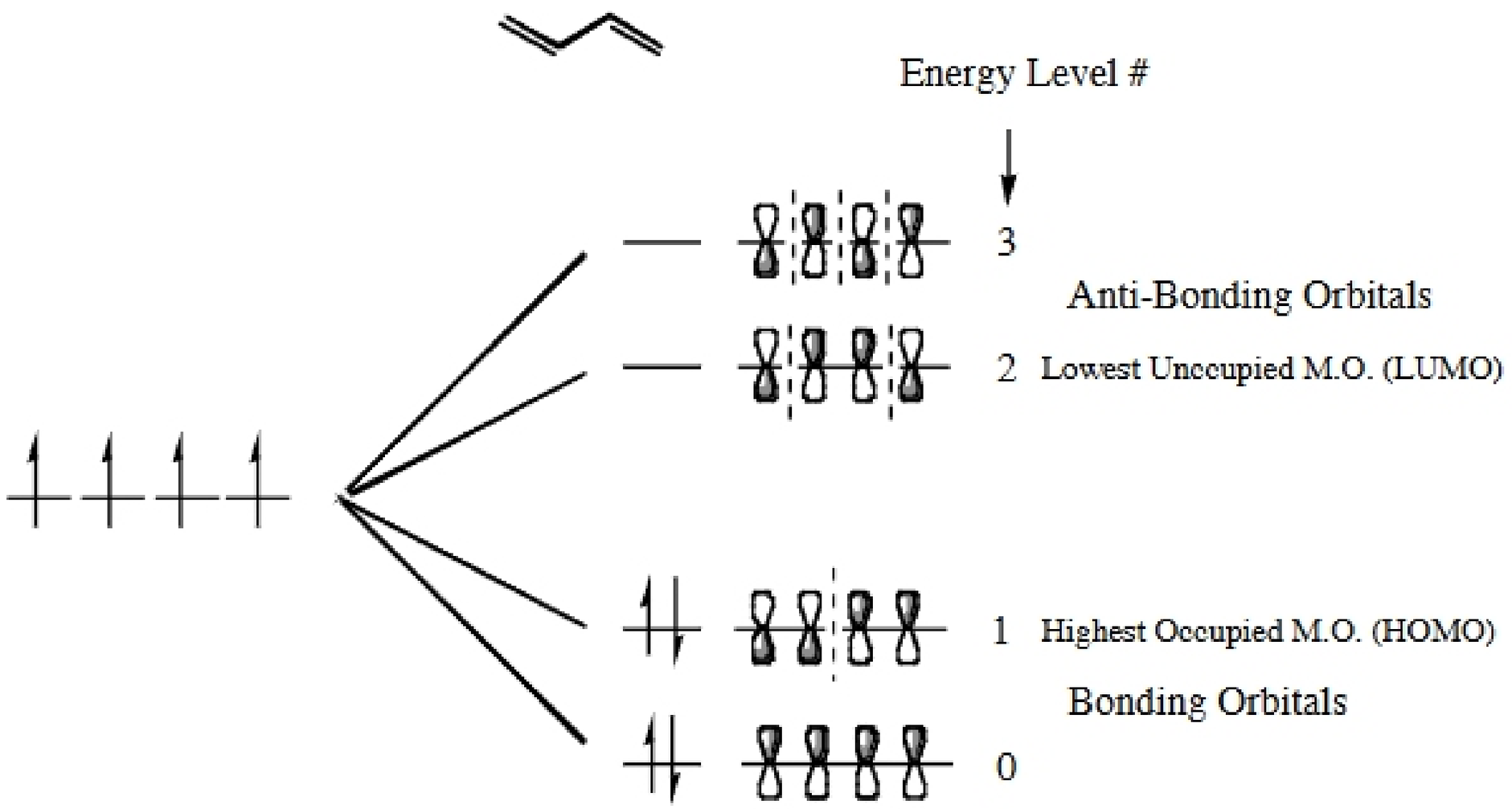
There are a lot of double bonds, but there is NO conjugation in this molecule.

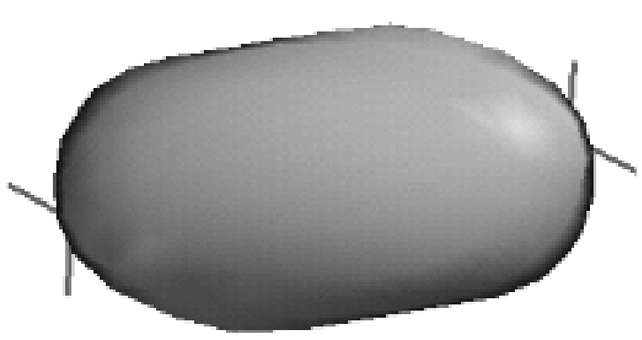
For linearly conjugated systems, it is quite straightforward to look at the molecular orbital picture of the various energy levels in the molecule. Here are a list of guidelines for the preparation of such a picture:

1) For every p-orbital, there is a π-molecular orbital.
2) Each molecular orbital (M.O.) has its own, unique energy associated with it.
3) For molecules with an even number of π-bonds, half of the M.O.'s are higher in energy than the starting p-orbitals, and half are lower in energy.
   For molecules with an odd number (n) of carbons in the conjugated framework (i.e. allyl radical), (n-1)/2 M.O.'s are higher in energy, (n-1)/2 are lower in energy, and there is ONE nonbonding M.O., with the same energy as the p-orbitals.
4) The lowest energy M.O. has 0 nodes. The highest energy M.O. has n-1 nodes, where n is the total number of M.O.'s.
5) The number of nodes increases by one for each higher energy level.
   a) M.O.'s with an odd number of nodes always have a node in the middle.
   b) M.O.'s with an even number of nodes NEVER have a node in the middle.
6) Each M.O. will hold 2 electrons.

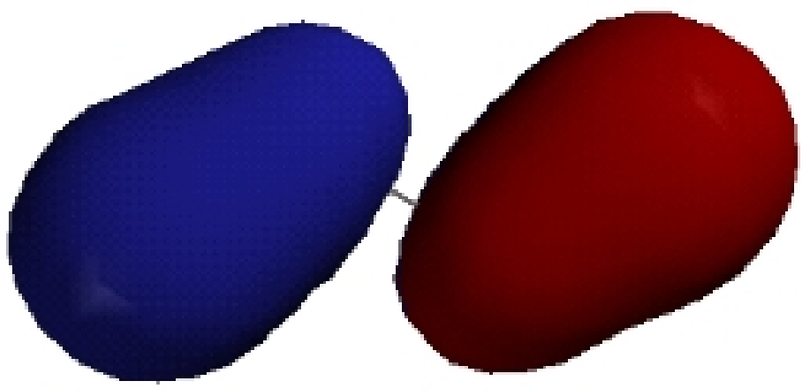
The MO diagram for butadiene is shown below. Things you should note:
1) the progression of nodes (from 0 to 1 to 2 to 3)

2) A filled set of bonding orbitals.
3) An EMPTY set of anti-bonding orbitals.
4) Electrons with PAIRED SPINS!
Below the MO diagram, I have put calculated Electron Density Plots for each M.O.

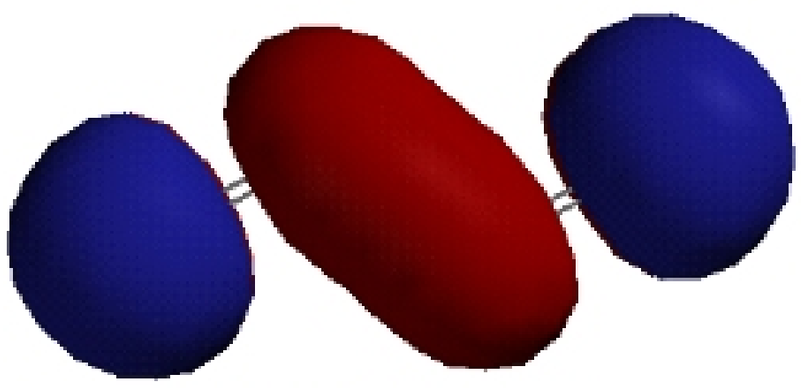




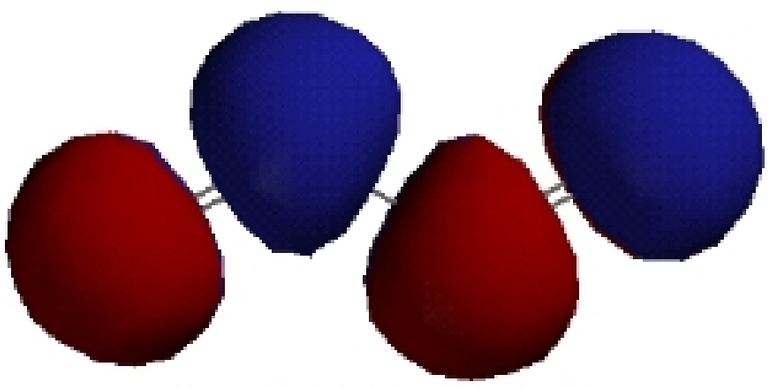
Level 0 (lowest energy)



Level 1 (HOMO)



Level 2 (LUMO)

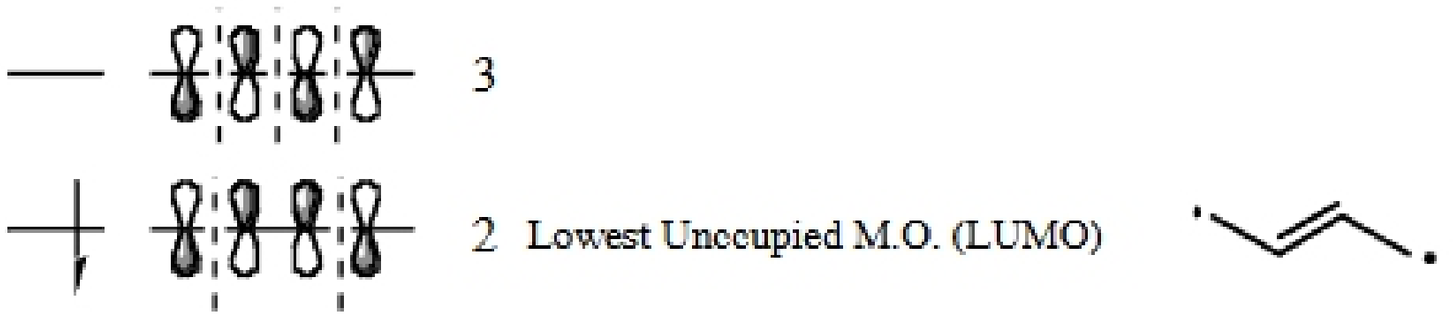


Level 3 (Highest Energy)

These plots show that the lowest energy level has electron density spread over the entire conjugated backbone. The HOMO looks more like two double bonds, and is the best representation of the way we write the structure, namely:  . The LUMO has its

double-bond character in the center of the molecule, while the Highest anti-bonding orbital shows NO interaction between any of the p-orbitals.

What if we put the molecule into its first excited state? The orbital diagram then looks like the diagram below. The actual structure of the molecule is best represented by the electron density shown in the LUMO diagram (above), yielding the diradical structure shown on the right. You should be able to derive structures such as this from the orbital pictures of the HOMO and LUMO of any M.O. diagram.

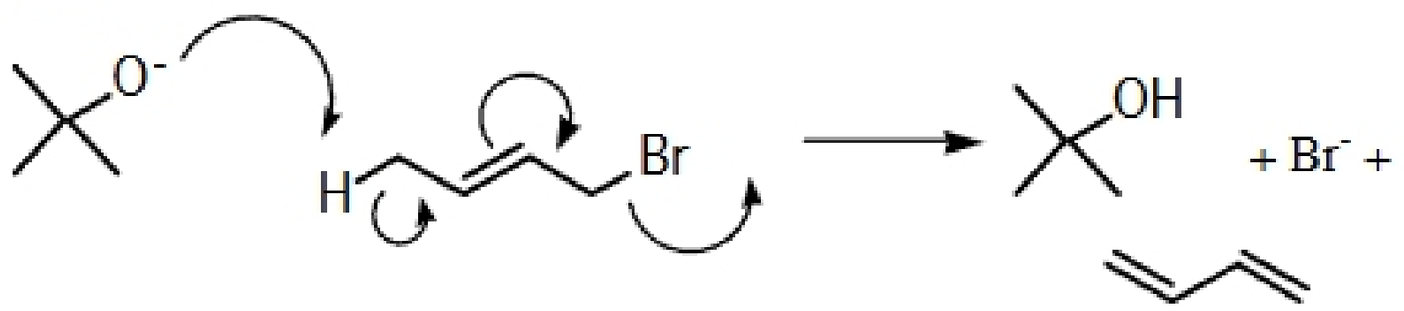


Preparation of Conjugated Systems:

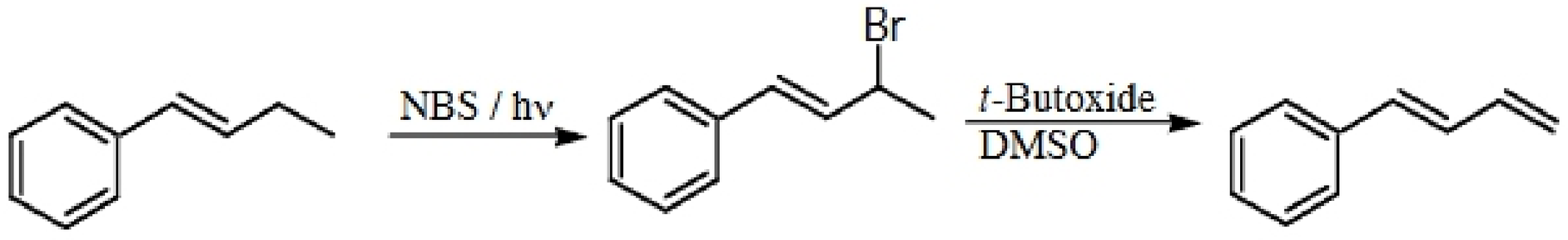
There are a number of methods for the preparation of conjugated systems. One possibility is by allylic bromination, followed by either normal (2) or conjugate (1) elimination:

1

Conjugate Elimination:



2



Reactions of Conjugated Systems:

As your text states, conjugated systems do not give simple products on addition of HX or X_2. Simply put, the charge generated from the initial electrophilic addition to one of the double bonds is delocalized over the entire conjugated system, leading to multiple products: