

Quickfire Challenge

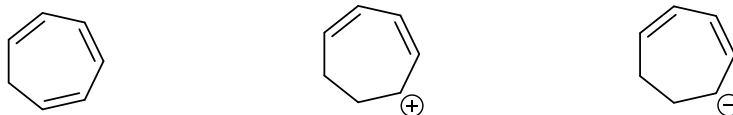
1. Briefly list the essential requirements for a conjugated pi system:
2. Examine the conjugated molecule below.



(all *trans*)-2,4,6-octatriene

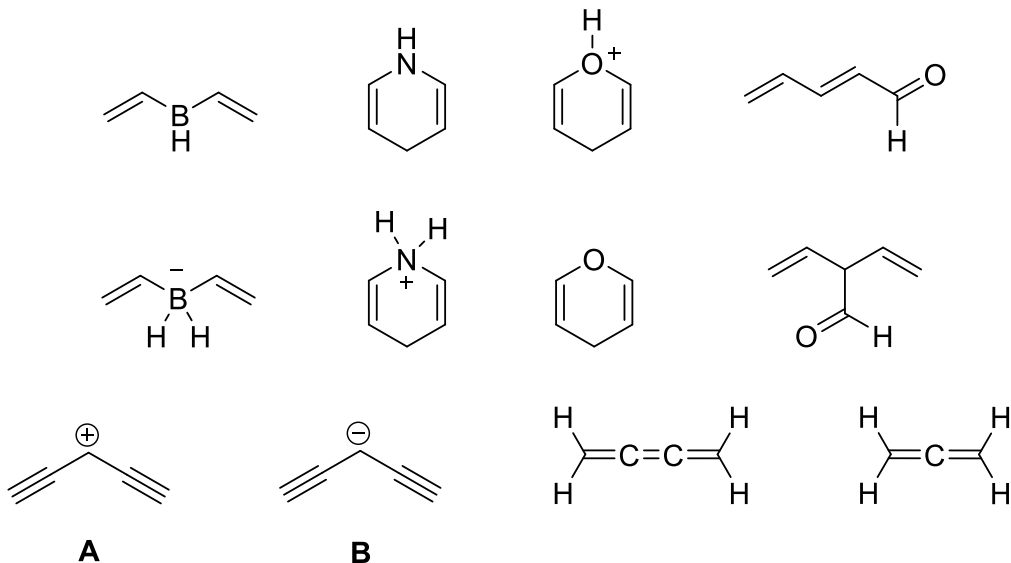
- a. Are all eight atoms in the octatriene involved in the conjugated pi system? Which ones are not? How do you know? Make a generalization about atoms that cannot be involved in pi systems.
- b. Draw the frontier molecular orbital (FMO) diagram for (all *trans*)-2,4,6-octatriene. Be sure to appropriately label all axes and relative energy levels. Elucidate how/where the FMO diagram indicates that conjugation is a stabilizing phenomenon.

3. While conjugation is relatively easy to recognize in simple linear chains of conjugated pi bonds, it can be difficult to see in more complicated systems such as those with heteroatoms, cations, anions, and/or cycles. One must diligently examine molecules according to the rules you listed in #1 and #2a above in order to determine the extent of conjugation. For example, examine the three conjugated pi systems below:

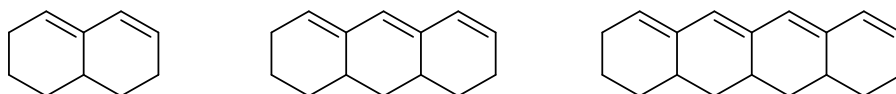


- a. Devise a stepwise strategy that will allow you to determine the number of atoms and electrons in complicated pi systems. Then apply your strategy to determine the number of atoms and electrons in each of the pi systems above.
- b. Hopefully, your strategy from #3a helped you conclude that each of the cycloheptene systems above are conjugated, yet differ in the number of atoms and/or electrons in their pi systems. If not, revise your strategy until you are able to arrive at the correct answers.
- c. Draw the frontier molecular orbital (FMO) diagrams for all three molecules above. Be sure to appropriately label all axes and relative energy levels. You should be able to “share” the same FMO for the cation and anion.

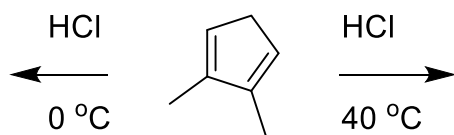
4. Using your revised strategy from #3a above, determine which of the molecules below are conjugated. For the ones that are conjugated, list (a) the number of atoms involved, (b) the number of atomic orbitals involved, (c) the number of molecular orbitals formed, and (d) the number of electrons involved. This is in lieu of drawing the full FMO diagrams.



5. Show how to synthesize **A** and **B** from #4 above, using any neutral starting material(s).
6. Electronic transitions at the HOMO-LUMO gap such as the ones responsible for the UV activity and visible color of many organic compounds are typically described in terms of wavelength (λ_{\max}) as opposed to energy.
- Are wavelength and energy inversely or directly proportional? Write the equation that quantifies their relationship.
 - Using your understanding of how conjugation impacts the HOMO-LUMO gap, rank the following compounds in order of increasing λ_{\max} and briefly rationalize your answer.



7. Draw the most likely products of the hydrohalogenation reactions of 2,3-dimethylcyclopenta-1,3-diene below:



8. When 1,4-dimethylcyclohepta-1,3-diene is treated with HBr at *any temperature*, only the 1,2-adduct is formed. None of the 1,4-adduct is observed. Provide a rational explanation for this observation.