

## AROMATIC COMPOUNDS

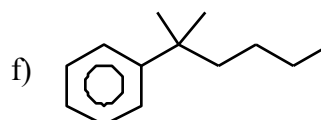
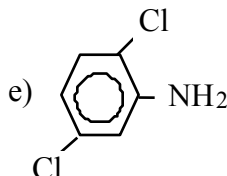
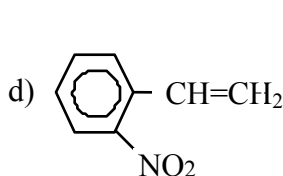
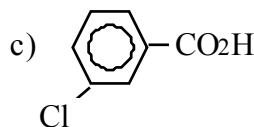
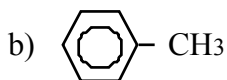
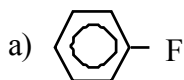
### A STUDENT SHOULD BE ABLE TO:

1. Name benzene derivatives given the structures, and draw the structures given the names.  
This includes:  
Monosubstituted benzenes named as derivatives of benzene: nitro, halo and alkyl. Also, anisole, aniline, toluene, phenol, benzaldehyde, acetophenone, benzoic acid; styrene, benzyl alcohol and benzyl halides.  
Compounds that are named by considering a phenyl or benzyl group as a substituent.  
Disubstituted benzenes, using both the *ortho/meta/para* system and the numerical system.  
Also, be able to recognize and draw xylenes and naphthalene.  
More highly substituted benzenes are always named using numbers.
2. Predict whether compounds and ions are aromatic, nonaromatic or antiaromatic.  
First check to see if the compound has a planar, cyclic pi system. If it's not cyclic, not planar, or has a tetrahedral atom in the ring, the ring is not aromatic. For our purposes, assume that a conjugated ring of 7 carbons or less must be planar.  
If it has a cyclic pi system, count the pi electrons. If there are  $4n + 2$  pi electrons ( $n$  is an integer, 0, 1, 2, 3 etc.) the compound is aromatic. (Hückel's Rule) If there are  $4n$  pi electrons, the compound is antiaromatic (especially unstable).  
Also, draw the potential energy diagram, and show the location of electrons on it, for compounds with monocyclic pi systems.
3. Predict the properties of aromatic compounds and ions. Especially, be able to compare and contrast aromatic, nonaromatic and antiaromatic species with respect to:  
Reaction type. Aromatic compounds undergo addition reactions with great difficulty or not at all. (Exception: Birch reduction)  
Relative stability (reactivity, resonance energy)  
Structure (relative bond lengths and angles, planarity). Also, be able to draw resonance structures having localized bonds given a structure with circles representing delocalized electrons.
4. Predict relative rates of reaction and positions of equilibria as well as other phenomena based on aromaticity changes.  
For reactions in which a nonaromatic species is converted to an aromatic one, the reaction will be favorable because the stability of the system increases.  
For reactions in which an aromatic species is converted to a nonaromatic one, the reaction will be unfavorable because the stability of the system decreases.  
Reactions in which the aromaticity doesn't change are normal reactions.
5. Predict the products for reactions occurring at the benzylic position, including: oxidation, free-radical bromination, substitution and elimination of benzylic halides. Carry out syntheses using these and other reactions.
6. Use the characteristic proton NMR signals of benzene and other aromatic ring protons and the characteristic reactions of benzene derivatives (e.g.,  $\text{Br}_2$  in  $\text{CCl}_4$  or  $\text{H}_2$  + catalyst) to predict whether or not an unknown compound is an alkene or a benzene derivative.

To best prepare for this module, please work Chapter 18 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 Name each of the following compounds.



1.2 Draw the structures of each of the following compounds.

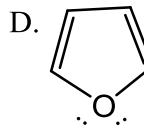
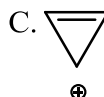
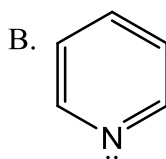
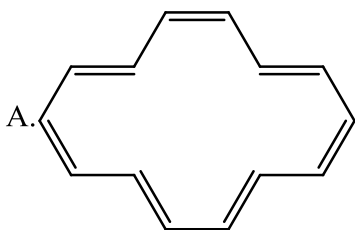
a) benzaldehyde

b) *p*-bromophenol

c) 2,4-dinitrotoluene

d) anisole

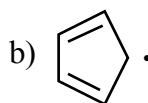
2.1 Which of the compounds shown is (are) aromatic?



2.2 Using complete sentences, explain the reasoning you used in deciding your answer for the last compound shown in 2.1 above.

2.3 Draw pi orbital energy level diagrams for each of the species indicated. Show the ground state electrons on each diagram.

a) Benzene



2.4 A monocyclic compound having a cyclic  $\pi$  system may be aromatic, nonaromatic or antiaromatic. What is the difference between the  $\pi$  orbital energy level diagrams?

3.1 Which of the following describes benzene?

- A. Hydrogenation occurs at room temperature and pressure.
- B. It undergoes addition reactions readily.
- C. All carbon-carbon bond lengths are the same in it.
- D. Its heat of hydrogenation per  $\pi$  bond is relatively high.

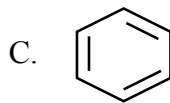
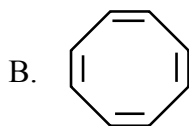
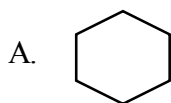
3.2 Compare and contrast benzene and cyclohexene with respect to each of the following.

a) Reaction with water in the presence of sulfuric acid.

b) Rate of reaction with hydrogen in the presence of a nickel catalyst.

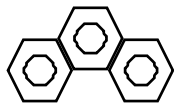
c) The amount of energy released for each hydrogen molecule added in a hydrogenation reaction.

3.3 Which of the following compounds contains the longest carbon-carbon bonds? Which one contains the shortest carbon-carbon bonds?

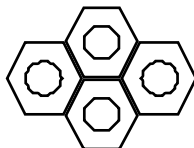


3.4 Draw a resonance structure having localized bonds for each of the following compounds. (Note: All 3 were found in the "Mars Rock" ALH84001, and are possibly evidence of past life on Mars.)

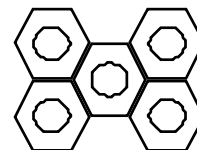
a) phenanthrene



b) pyrene

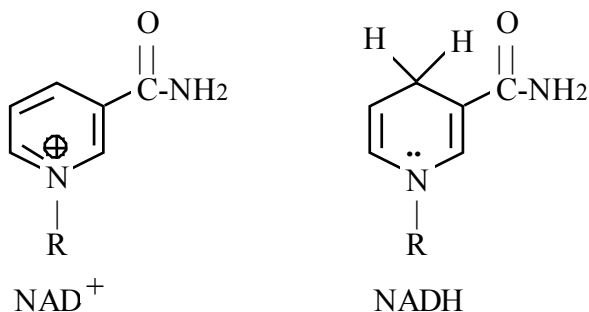


c) perylene

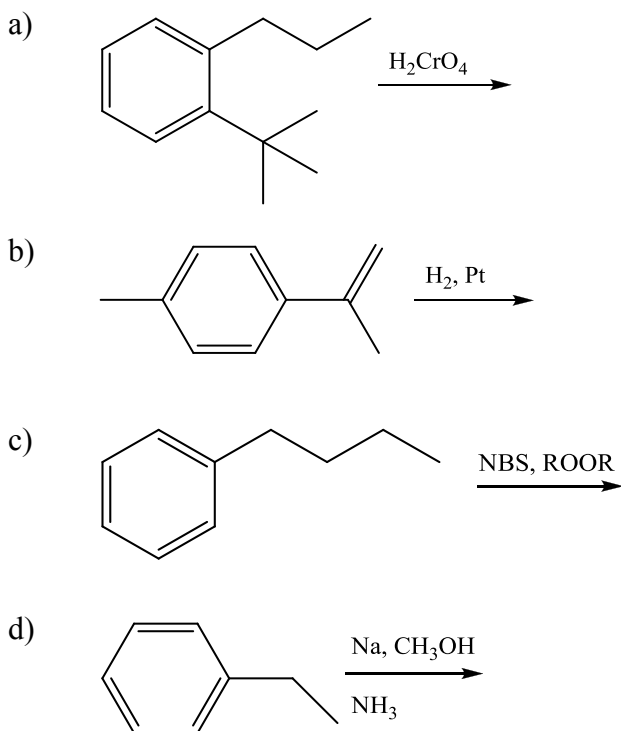


4.1 Cyclopentadiene is a much stronger acid than cycloheptatriene. Explain the reason for this, using equations and complete sentences.

- 4.2 Nicotinamide adenine dinucleotide is a coenzyme used by biological systems as an energy source. Conversion between oxidized and reduced forms of the coenzyme either releases energy for biochemical reactions or stores the energy of a reaction for subsequent use. The relevant portions of the oxidized form ( $\text{NAD}^+$ ) and the reduced form ( $\text{NADH}$ ) are shown below. Using complete sentences, explain which form of the coenzyme stores the energy, giving the reason for your choice.



- 5.1 Predict the product(s) of these reactions, or write “no reaction”.

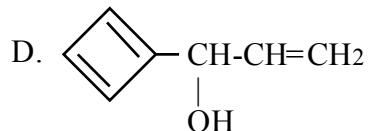
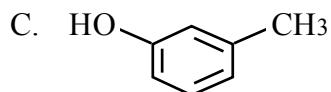
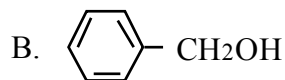
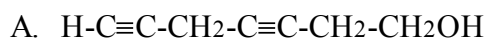


- 5.2 Propose a reasonable synthesis:

a) benzylamine from toluene

b) styrene from ethylbenzene

6.1 For the questions below, choose the answers from among the following set of compounds.



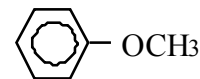
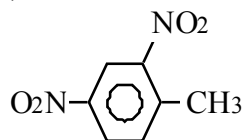
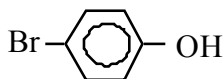
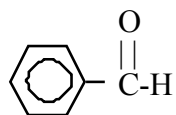
- a) Which of these compounds does not decolorize  $\text{Br}_2$  in  $\text{CCl}_4$  and gives a proton NMR spectrum containing a multiplet from between  $7\delta$  and  $8\delta$  from 5 hydrogens?
- b) Which of these compounds gives a brown precipitate when treated with  $\text{KMnO}_4$  and an aldehyde when reacted with PCC?
- c) Which of these compounds gives a multiplet between  $7\delta$  and  $8\delta$  in its proton NMR spectrum and no reaction with chromic acid?

6.2 Predict the  $^1\text{H}$  NMR spectrum you would observe for *p*-ethylanisole

## SOLUTIONS TO SAMPLE PROBLEMS:

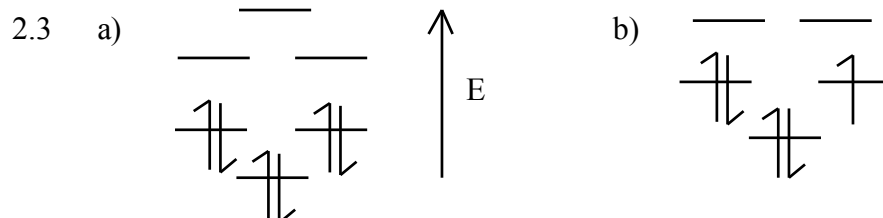
- 1.1 a) fluorobenzene b) toluene c) *m*-chlorobenzoic acid or 3-chlorobenzoic acid  
d) *o*-nitrostyrene or 2-nitrostyrene  
e) 2,5-dichloroaniline f) 2-methyl-2-phenylhexane.

- 1.2 a) benzaldehyde b) *p*-bromophenol c) 2,4-dinitrotoluene d) anisole



- 2.1 All four are aromatic.

- 2.2 The compound has a cyclic pi system. It contains two pi bonds. Since there is no pi bond on the oxygen, one of the pairs of electrons on the O is a part of the cyclic pi system. There are six pi electrons in the ring, and it is therefore aromatic.



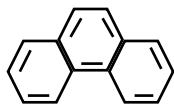
- 2.4 In aromatic compounds, the occupied orbital or orbitals having the highest energy are completely filled with electrons. The first diagram above is an example. In benzene, the two electron-containing orbitals having the highest energy are completely filled with four electrons. In the nonaromatic cyclopentadienyl radical b, the two electron-containing orbitals having the highest energy contain only three electrons. In an antiaromatic compound, the highest occupied molecular orbitals each have one electron, so the compound is especially unstable.

- 3.1 C

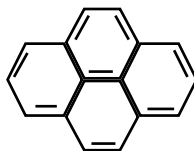
- 3.2 a) In the presence of sulfuric acid, cyclohexane reacts with water to form cyclohexanol. This is an addition reaction (hydration). Benzene will not undergo this addition reaction because it is aromatic, and reaction would lead to a nonaromatic product.  
b) Both compounds react with hydrogen ( $H_2$ ) in the presence of nickel. However, benzene only undergoes the reaction slowly at high temperature and pressure.  
c) Upon hydrogenation, cyclohexene releases  $120 \text{ kJ mol}^{-1}$  of energy. Benzene might be expected to release  $3 \times 120$  or  $360 \text{ kJ mol}^{-1}$ , but it releases only  $208 \text{ kJ mol}^{-1}$ . This is  $(360 - 208) / 3$  or  $69.3 \text{ kJ mol}^{-1}$  of energy less per mole of  $H_2$  added. (It is not important that you know the precise numbers. You should know that, because benzene is aromatic, it is much more stable than a hypothetical alkene with the same formula. Since it has lower energy to start with, it does not release as much energy when hydrogenated.)

3.3 longest A; shortest B

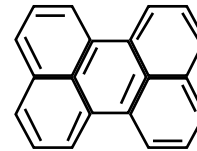
3.4 a) phenanthrene



b) pyrene

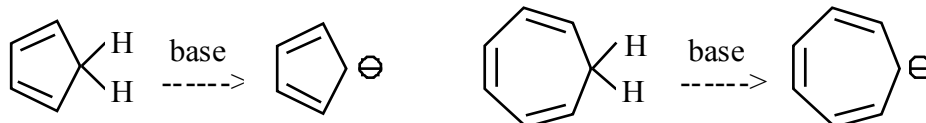


c) perylene



Note: All of these problems have several correct answers. In all of them, there is one (not more, not less) pi bond to each carbon atom in the rings that have circles in them.

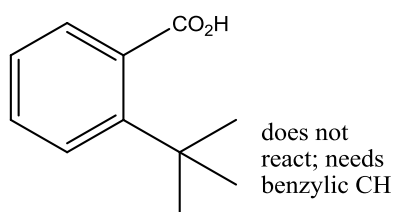
4.1 First, here are equations for the two compounds acting as acids:



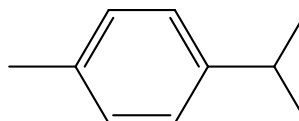
Neither starting material is aromatic (both have tetrahedral atoms). The conjugate base of cyclopentadiene is aromatic; it is therefore predicted that this conjugate base will be stable and easy to form (that is, cyclopentadiene is a relatively strong acid). The conjugate base of cycloheptatriene is antiaromatic.

4.2  $\text{NAD}^+$  is aromatic and NADH is not. When  $\text{NAD}^+$  is reduced to NADH, it goes from a more stable aromatic species to a less stable nonaromatic species. The less stable NADH is higher in energy, so it must gain energy for this transformation to occur. When the reverse transformation from NADH to  $\text{NAD}^+$  occurs, the energy is released when the more stable aromatic species is formed. It is the nonaromatic NADH that stores the energy. (The energy used to convert  $\text{NAD}^+$  to NADH is stored in the NADH as potential energy).

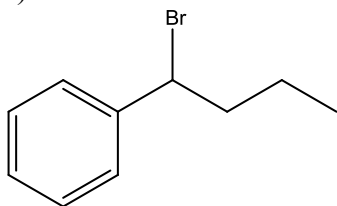
5. a)



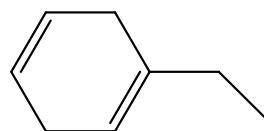
b)



c)

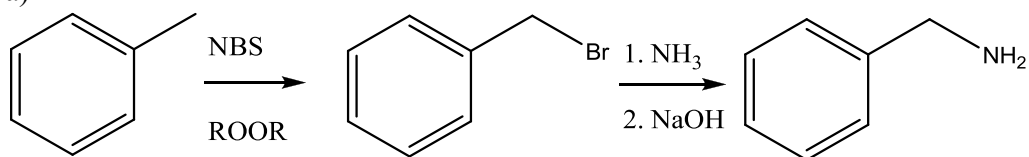


d) selective for this isomer

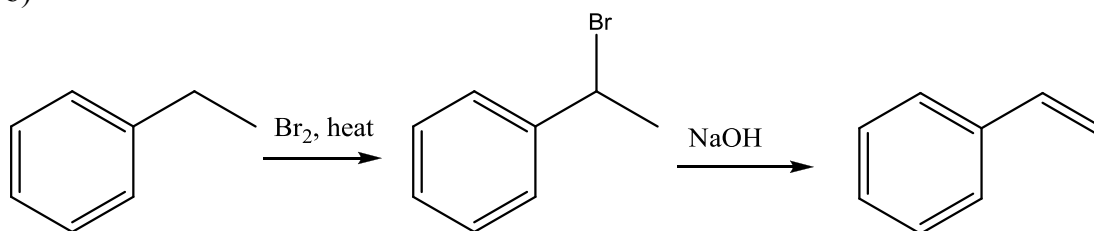


5.2

a)



b)



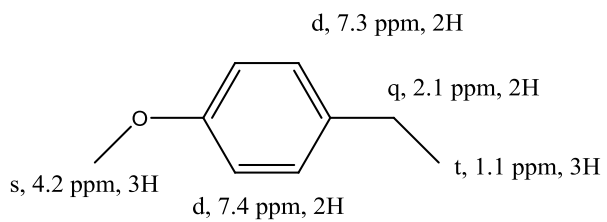
6.1

a) B

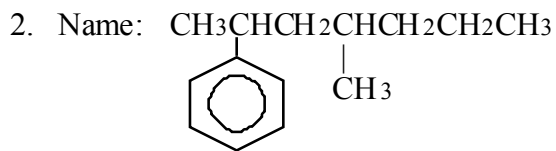
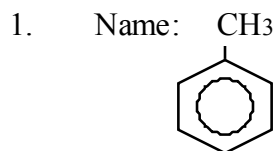
b) A

c) C

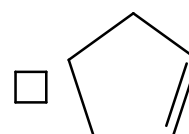
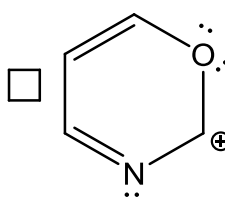
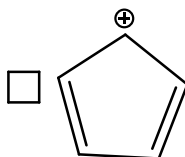
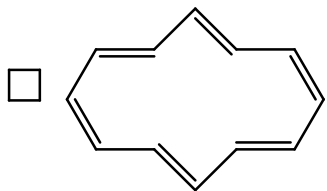
6.2



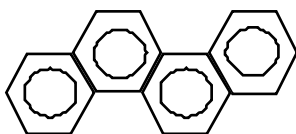




5. Which of the following is (are) aromatic? Put an x in the box(es) next to those that are.



6. Draw a resonance structure (having localized bonds) for chrysene.

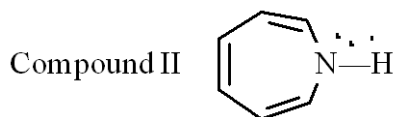
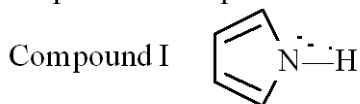


7. Draw a pi orbital energy level diagram for cyclobutadiene (its structure is shown), and indicate the locations of the ground state electrons on it.



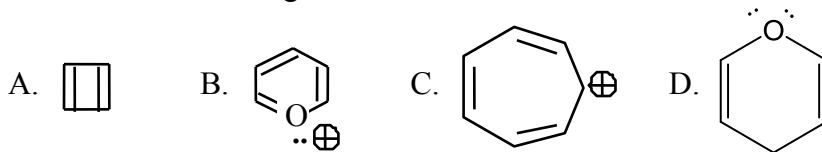
Potential  
Energy

8. The reaction of compound I with acid occurs much less readily than the same reaction of compound II. Explain the reason for this, using complete sentences.



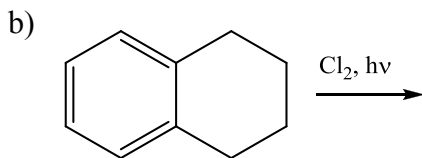
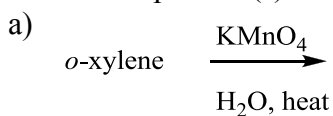
9. Propose a synthesis of 1-phenyl-1-propanol from propylbenzene

1. Which of the following is/are aromatic?

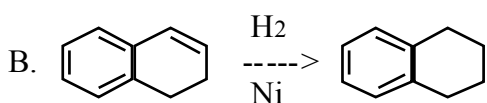
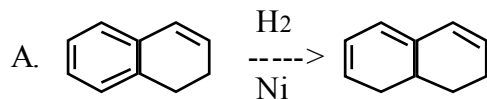


2. Draw the potential energy diagram for the cation C in problem 1, and show the ground state  $\pi$  electron configuration.

3. Predict the product(s)

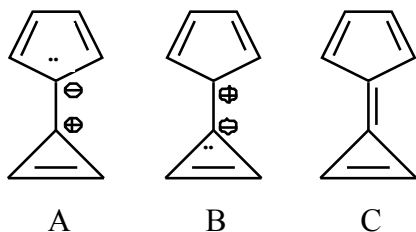


4. Which of these reactions requires more energy?

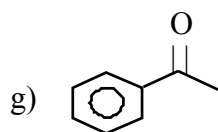
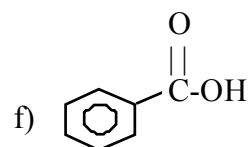
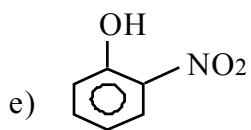
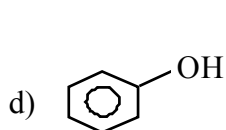
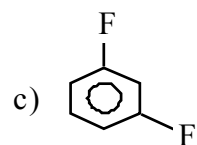
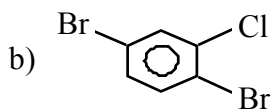
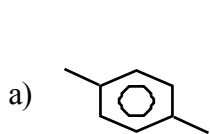


Answer: \_\_\_\_\_

5. The compound below is called calixene. It is polar; the five-membered ring is the negative end of the dipole and the three-membered ring is the positive end. Two less important resonance contributors of calixene are shown also. Why is the actual molecule polarized as in structure A and not B or C?



6. Name each of the following compounds.

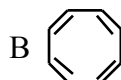
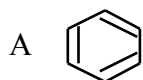


7. Draw structures for each of the following compounds.

a) *p*-bromobenzyl alcohol

b) 3,4-dinitrobenzoic acid

8. Indicate which of these two compounds each of the following statements applies to by placing the appropriate letter in each blank.



- \_\_\_\_\_ reacts with Br<sub>2</sub> in CCl<sub>4</sub>, cold, dark
- \_\_\_\_\_ does not react with cold, dilute KMnO<sub>4</sub>
- \_\_\_\_\_ is not a planar molecule
- \_\_\_\_\_ does not undergo hydration in aqueous acid