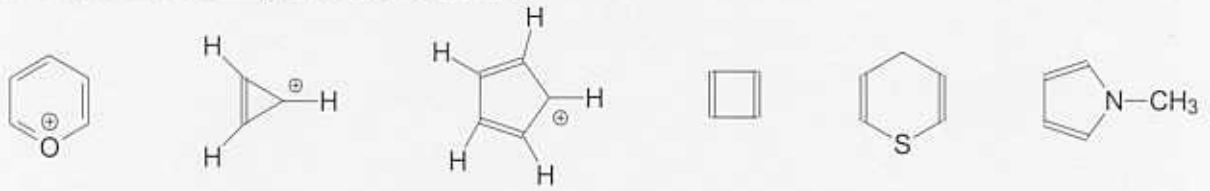
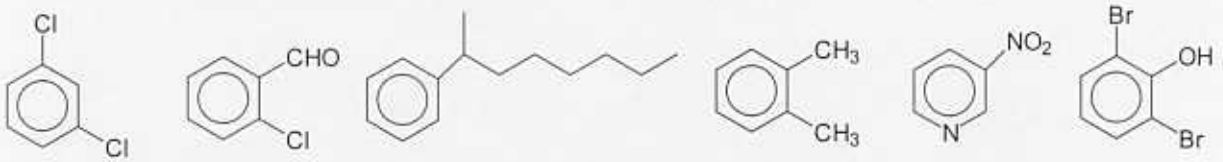
Problem Set Chapter 15

1. Which of the following molecules are aromatic?



a b c d e f

2. Name the following compounds:



a b c d e f

3. The compound shown below has an extremely high dipole moment because one of is resonance forms is aromatic. Show this resonance form, don't forget about charges!

4. Show valid structural formulas for the following:
a. 2-choroaniline, b. *meta*-xylene, c. 3,5-dibromobenzoic acid, d. 2-chlorofuran, e. *para*-chlorobenzaldehyde

5. Most hydrocarbons are extremely weak acids. Cyclopentadiene, however, is an exception and is partially deprotonated even in aqueous sodium hydroxide solution. Show a reaction equation for this reaction and explain the high acidity of cyclopentadiene!

6. The ^{1}H NMR spectrum of [14]annulene at –60°C shows two signals, one at 0 ppm and one at 7.6 ppm. a) Is this compound aromatic? b) Which protons give rise to the two NMR signals and what is their ratio?

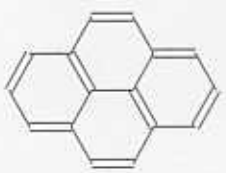
[14]annulene

7. Reaction a) procedes easily while reaction b) does not. Account for this fact by first suggesting a plausible mechanism for a) and then explaining why it will fail for b).

a b

8. How many proton NMR signals corresponding to non-equivalent kinds of protons would you expect for:
a. [18]annulene, b. benzene, c. the cyloheptatrienyl cation, d. the cyclopentadienyl anion, e. 1,3,5-trimethylbenzene.

9. The compound below has been shown to be aromatic. Does it abide by Huckel's rule? Interpret your findings!



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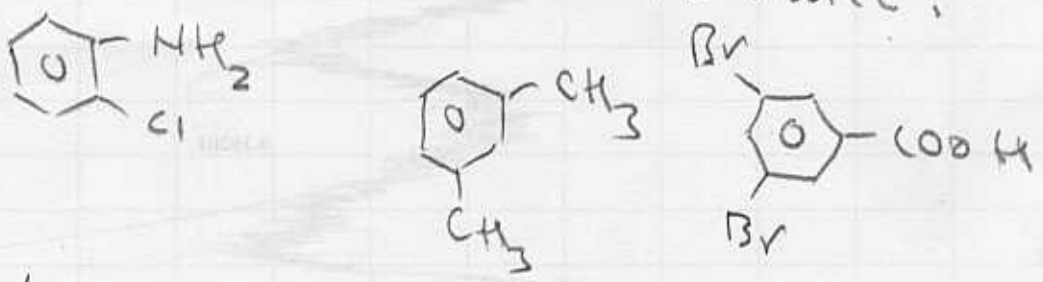
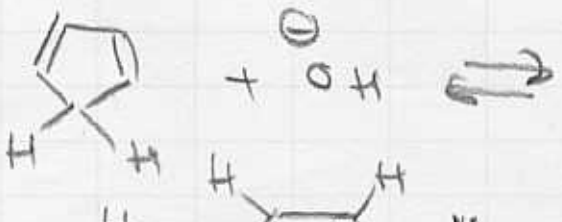
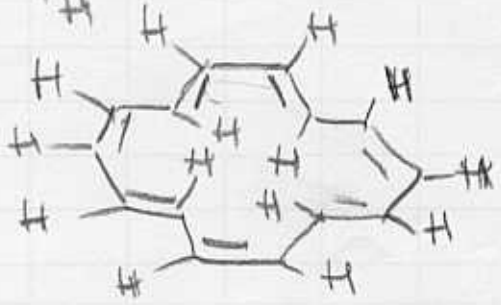
1) a, b and f are aromatic

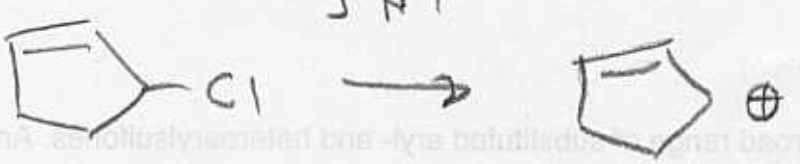
2) a 1,3 - dichlorobenzene (or meta)
   b 2- chlorobenzaldehyde (or ortho)
   c 2- phenyloctane
   d o- xylene
   e 3- nitropyridine
   f 2,6- dibromophenol

3) 
both rings are aromatic!

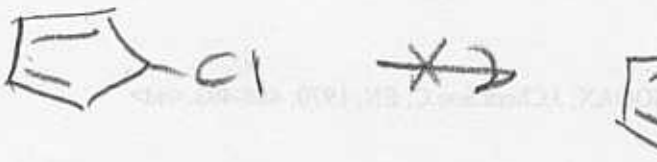
4) 

5) 
← aromatic!

6) 
10 H's outside at 7.6
4 H's inside at 0
ratio 2:5

7) 

allylic cation, very stable



anti aromatic!

8) a – 2 b – 1 c – 1 d – 1 e – 2

9) 16 π electrons, should be anti-aromatic according to Hückel.

→ Hückel only strictly applies to <u>mono</u> cyclic compounds.