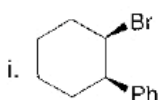
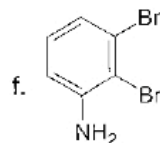
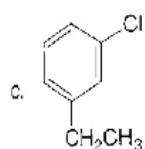
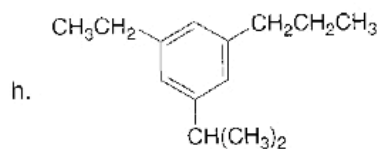
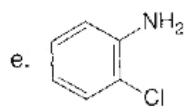
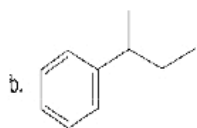
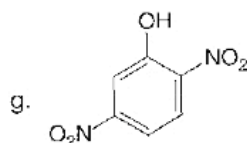
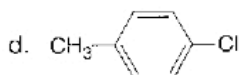
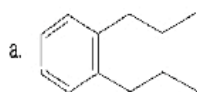


## nomenclature

124 Give the IUPAC name for each compound.



125 Draw a structure corresponding to each name.

a. *p*-dichlorobenzene

e. 2,6-dimethoxytoluene

b. *m*-chlorophenol

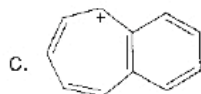
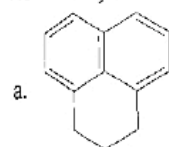
f. 2-phenyl-1-butene

c. *p*-iodoaniline

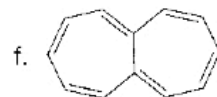
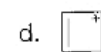
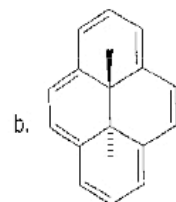
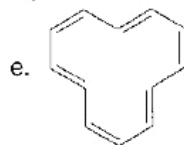
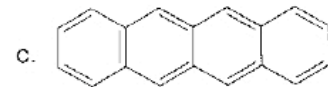
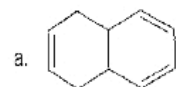
g. 2-phenyl-2-propen-1-ol

d. *o*-bromonitrobenzeneh. *trans*-1-benzyl-3-phenylcyclopentane126 Draw and name all the isomeric trichlorobenzenes (molecular formula  $C_6H_3Cl_3$ ).

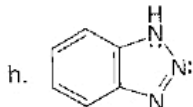
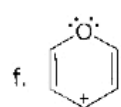
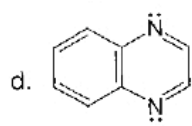
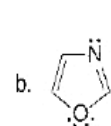
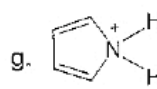
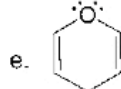
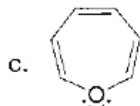
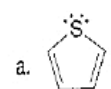
## aromaticity

127 How many  $\pi$  electrons are contained in each molecule?

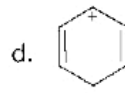
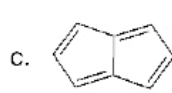
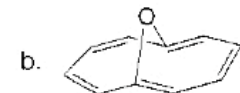
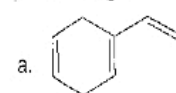
128 Which of the following compounds are aromatic? For any compound that is not aromatic, state why this is so.



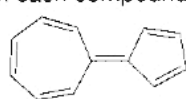
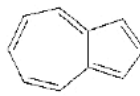
129 Which of the following heterocycles are aromatic?



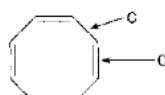
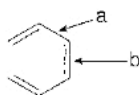
130 Label each compound as aromatic, antiaromatic, or not aromatic. Assume all completely conjugated compounds have planar rings.



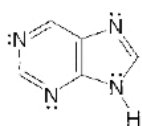
- 17.31 Hydrocarbons **A** and **B** both possess a significant dipole, even though each is composed only of C–C and C–H bonds. Explain why the dipole arises in each compound. Use resonance structures to illustrate the direction of the dipole. Which ring is more electron rich in each compound?

**A**azulene  
**B**

- 17.32 Rank the indicated C–C bonds in order of increasing bond length, and explain why you chose this order.



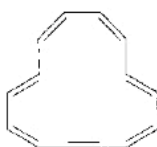
- 17.33 The purine heterocycle occurs commonly in the structure of DNA.



purine

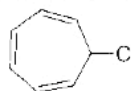
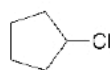
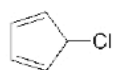
- How is each N atom hybridized?
- In what type of orbital does each lone pair on a N atom reside?
- How many  $\pi$  electrons does purine contain?
- Why is purine aromatic?

- 17.34

**C**

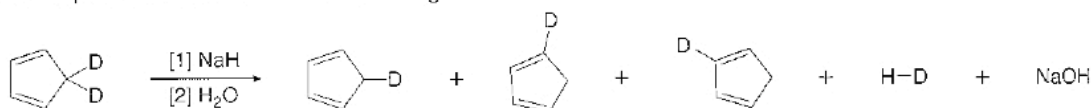
- How many  $\pi$  electrons does **C** contain?
- How many  $\pi$  electrons are delocalized in the ring?
- Explain why **C** is aromatic.

- 17.35 Explain the observed rate of reactivity of the following 2° alkyl halides in an  $S_N1$  reaction.

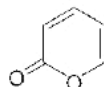


Increasing reactivity

- 17.36 Draw a stepwise mechanism for the following reaction.



- 17.37 Explain why  $\alpha$ -pyrone reacts with  $\text{Br}_2$  to yield a substitution product (like benzene does), rather than an addition product to one of its C=C bonds.

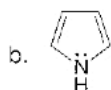
 $\alpha$ -pyrone

## Resonance

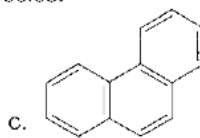
- 17.38 Draw additional resonance structures for each species.



cyclopropenyl radical

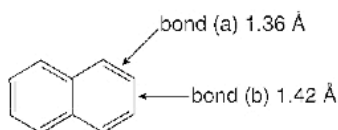


pyrrole



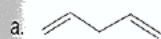
phenanthrene

- 17.39 The carbon–carbon bond lengths in naphthalene are not equal. Use a resonance argument to explain why bond (a) is shorter than bond (b).



## Acidity

17.40 Which compound in each pair is the stronger acid?



and



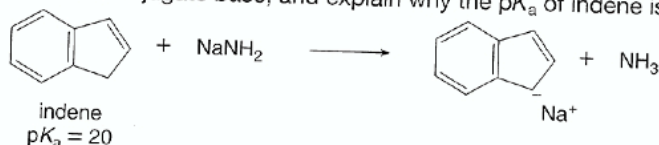
b.



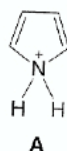
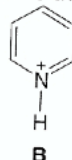
and



17.41 Treatment of indene with  $\text{NaNH}_2$  forms its conjugate base in a Brønsted–Lowry acid–base reaction. Draw all reasonable resonance structures for indene's conjugate base, and explain why the  $\text{p}K_a$  of indene is lower than the  $\text{p}K_a$  of most hydrocarbons.

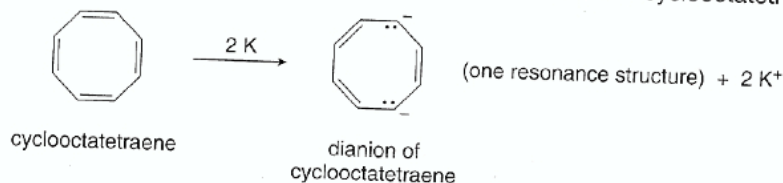


17.42 Explain why **A** (the conjugate acid of pyrrole) is much more acidic than **B** (the conjugate acid of pyridine).

 $\text{p}K_a = 0.4$  $\text{p}K_a = 5.2$ 

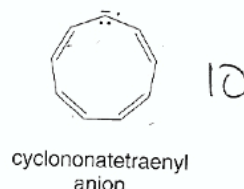
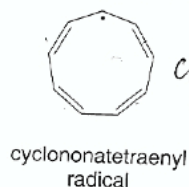
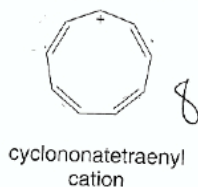
## Inscribed Polygon Method

17.43 Use the inscribed polygon method to show the pattern of molecular orbitals in cyclooctatetraene.



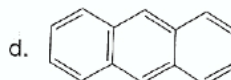
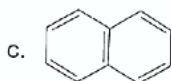
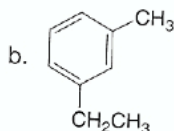
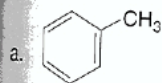
- Label the MOs as bonding, antibonding, or nonbonding.
- Indicate the arrangement of electrons in these orbitals for cyclooctatetraene, and explain why cyclooctatetraene is not aromatic.
- Treatment of cyclooctatetraene with potassium forms a dianion. How many  $\pi$  electrons does this dianion contain?
- How are the  $\pi$  electrons in this dianion arranged in the molecular orbitals?
- Classify the dianion of cyclooctatetraene as aromatic, antiaromatic, or not aromatic, and explain why this is so.

17.44 Use the inscribed polygon method to show the pattern of molecular orbitals in 1,3,5,7-cyclononatetraene and use it to label its cation, radical, and anion as aromatic, antiaromatic, or not aromatic.



## Spectroscopy

17.45 How many  $^{13}\text{C}$  NMR signals does each compound exhibit?



17.46 Which of the diethylbenzene isomers (ortho, meta, or para) corresponds to each set of  $^{13}\text{C}$  NMR spectral data?

[A]  $^{13}\text{C}$  NMR (ppm)

16  
29  
125  
127.5  
128.4  
144

[B]  $^{13}\text{C}$  NMR (ppm)

15  
26  
126  
128  
142

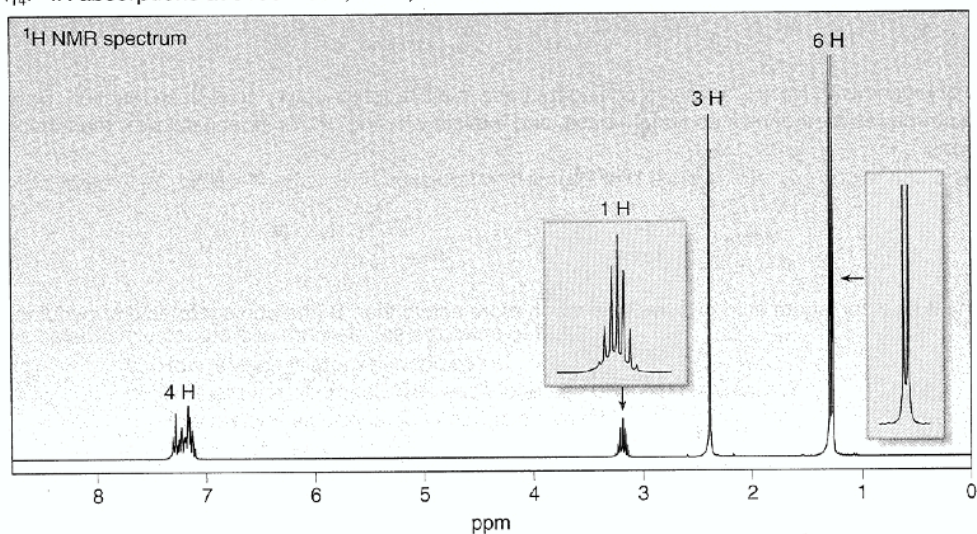
[C]  $^{13}\text{C}$  NMR (ppm)

16  
29  
128  
141

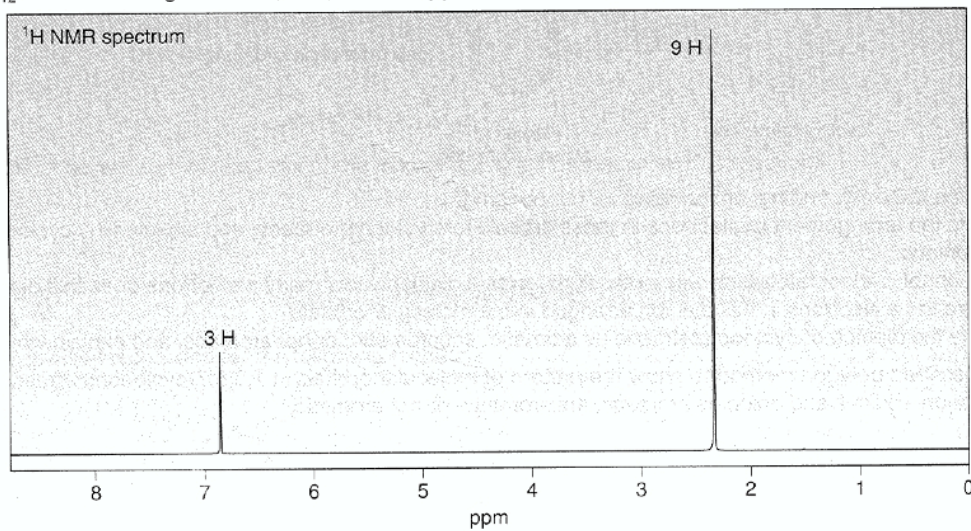


17.47 Propose a structure consistent with each set of data.

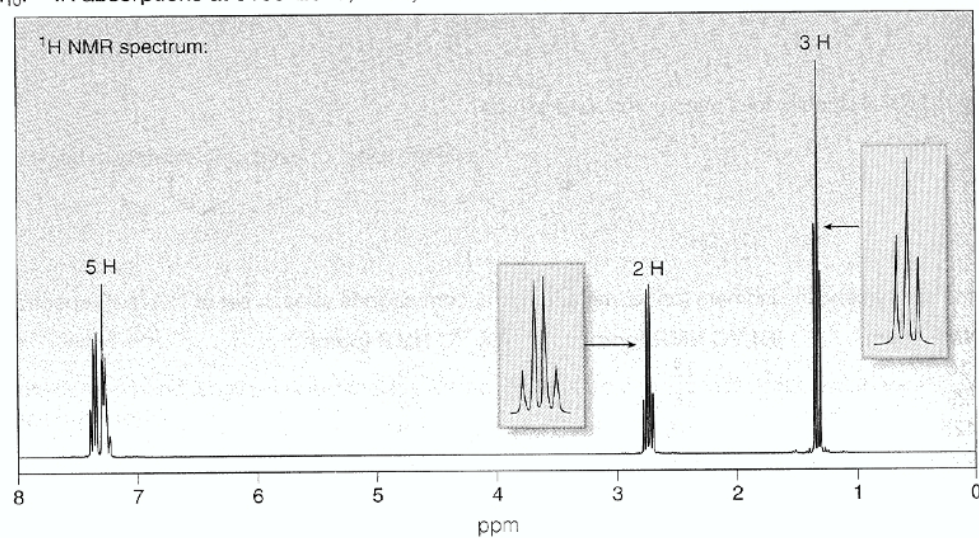
a.  $C_{10}H_{14}$ : IR absorptions at 3150–2850, 1600, and 1500  $cm^{-1}$ .



b.  $C_9H_{12}$ :  $^{13}C$  NMR signals at 21, 127, and 138 ppm.



c.  $C_8H_{10}$ : IR absorptions at 3108–2875, 1606, and 1496  $cm^{-1}$ .



17.48 Propose a structure consistent with each set of data.

a. Compound **A**:

Molecular formula:  $C_8H_{10}O$

IR absorption at  $3150\text{--}2850\text{ cm}^{-1}$

$^1H$  NMR data: 1.4 (triplet, 3 H), 3.95 (quartet, 2 H), and 6.8–7.3 (multiplet, 5 H) ppm

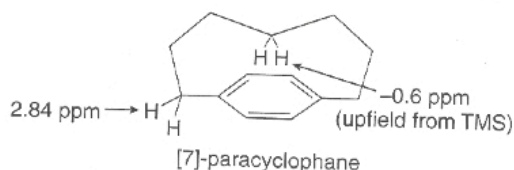
b. Compound **B**:

Molecular formula:  $C_9H_{10}O_2$

IR absorption at  $1669\text{ cm}^{-1}$

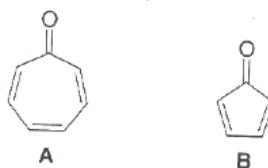
$^1H$  NMR data: 2.5 (singlet, 3 H), 3.8 (singlet, 3 H), 6.9 (doublet, 2 H) and 7.9 (doublet, 2 H) ppm

17.49 [7]-Paracyclophane is an unusual aromatic compound with a bridge connecting two para carbons. Explain why the labeled protons absorb in different regions of the  $^1H$  NMR spectrum, even though both are bonded to  $sp^3$  hybridized C atoms.

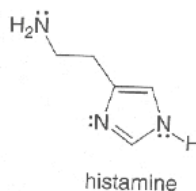


### Challenge Problems

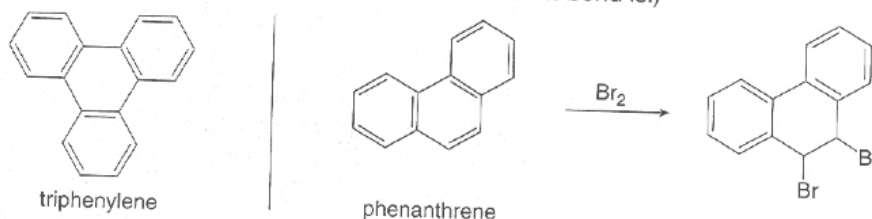
17.50 Explain why compound **A** is much more stable than compound **B**.



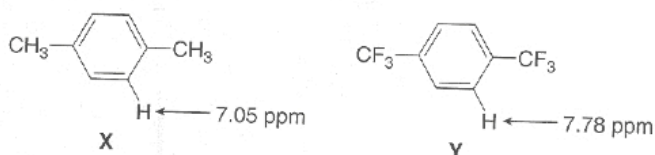
17.51 Rank the N atoms in histamine in order of increasing basicity.



17.52 Explain why triphenylene resembles benzene in that it does not undergo addition reactions with  $Br_2$ , but phenanthrene reacts with  $Br_2$  to yield the addition product drawn. (Hint: Draw resonance structures for both triphenylene and phenanthrene, and use them to determine how delocalized each  $\pi$  bond is.)



17.53 Although benzene itself absorbs at 7.3 ppm in its  $^1H$  NMR spectrum, the protons on substituted benzenes absorb either upfield or downfield from this value, depending on the substituent. Explain the observed values for the para disubstituted benzene derivatives **X** and **Y**.



Then explain why *p*-difluorobenzene shows a single peak in its  $^1H$  NMR spectrum at 7.00 ppm.