

## Chapter 15 – Benzene and Aromaticity

### Chapter Outline

- I. Introduction to aromatic compounds (Sections 15.1 – 15.2).
  - A. Sources of aromatic hydrocarbons (Section 15.1).
    1. Some aromatic hydrocarbons are obtained from distillation of coal tar.
    2. Other aromatic hydrocarbons are formed when petroleum is passed over a catalyst during refining.
  - B. Naming aromatic compounds.
    1. Many aromatic compounds have nonsystematic names.
    2. Monosubstituted benzenes are named in the same way as other hydrocarbons, with -benzene as the parent name.
      - a. Alkyl-substituted benzenes are named in two ways:
        - i. If the alkyl substituent has six or fewer carbons, the hydrocarbon is named as an alkyl-substituted benzene.
        - ii. If the alkyl substituent has more than six carbons, the compound is named as a phenyl-substituted alkane.
      - b. The  $\text{C}_6\text{H}_5\text{CH}_2-$  group is a benzyl group.
    3. Disubstituted benzenes are named by the ortho(*o*), meta(*m*), para(*p*) system.
      - a. A benzene ring with two substituents in a 1,2 relationship is *o*-disubstituted.
      - b. A benzene ring with two substituents in a 1,3 relationship is *m*-disubstituted.
      - c. A benzene ring with two substituents in a 1,4 relationship is *p*-disubstituted.
      - d. The *o*, *m*, *p*-system of nomenclature is also used in describing reactions.
    4. Benzenes with more than two substituents are named by numbering the position of each substituent.
      - a. Number so that the lowest possible combination of numbers is used.
      - b. Substituents are listed alphabetically.
    5. Any of the nonsystematic names can be used as a parent name.
  - C. Structure and stability of benzene (Section 15.2).
    1. Stability of benzene.
      - a. Benzene doesn't undergo typical alkene reactions.
      - b. Benzene reacts slowly with  $\text{Br}_2$  to give substitution, not addition, product.
      - c.  $\Delta H^\circ_{\text{hydrog}}$  of benzene is 150 kJ/mol less than that predicted for 3 x  $\Delta H^\circ_{\text{hydrog}}$  of cyclohexene, indicating that benzene has extra stability.
    2. Structure of benzene.
      - a. All carbon-carbon bonds of benzene have the same length.
      - b. The electron density in all bonds is identical.
      - c. Benzene is planar, with all bond angles  $120^\circ$ .
      - d. All carbons are  $sp^2$ -hybridized and identical, and each carbon has an electron in a *p* orbital perpendicular to the plane of the ring.
      - e. Resonance theory explains that benzene is a resonance hybrid of two forms.
      - f. Benzene is represented in this book as one line-bond structure, rather than as a hexagon with a circle to represent the double bonds.
    3. Molecular orbital picture of benzene.
      - a. It is impossible to define 3 localized  $\pi$  bonds; the electrons are delocalized over the ring.
      - b. Six molecular orbitals (MOs) can be constructed for benzene.
        - i. The 3 lower-energy MOs are bonding MOs.
        - ii. The 3 higher energy MOs are antibonding.
        - iii. One pair of bonding orbitals is degenerate, as is one pair of antibonding orbitals.

- iv. The 6 bonding electrons of benzene occupy the 3 bonding orbitals and are delocalized over the ring.

## II. Aromaticity (Sections 15.3 – 15.7).

### A. The Hückel $4n + 2$ rule (Section 15.3).

1. For a compound to be aromatic, it must possess the qualities we have already mentioned and, in addition, must fulfill Hückel's Rule.
2. Hückel's Rule: A molecule is aromatic only if it has a planar, monocyclic system of conjugation with a total of  $4n + 2 \pi$  electrons (where  $n$  is an integer).
3. Molecules with (4, 8, 12 ...)  $\pi$  electrons are antiaromatic.
4. Examples:
  - a. Cyclobutadiene ( $n = 4$ ) is antiaromatic.
  - b. Benzene ( $n = 6$ ) is aromatic.
  - c. Planar cyclooctatetraene ( $n = 8$ ) is antiaromatic.
    - i. Cyclooctatetraene is stable, but its chemical behavior is like an alkene, rather than an aromatic compound.
    - ii. Cyclooctatetraene is tub-shaped, and its bonds have two different lengths.

### B. Aromatic ions (Section 15.4).

1. Any cyclic conjugated molecule with  $4n + 2$  electrons can be aromatic, even if it is an ion.
2. The cyclopentadienyl anion.
  - a. Although cyclopentadiene isn't aromatic, removal of  $H^+$  produces a six- $\pi$ -electron cyclic anion that is aromatic.
  - b. Cyclopentadiene has a  $pK_a = 16$ , indicating that a stable anion is formed on removal of  $H^+$ .
  - c. Both the cyclopentadienyl cation (4  $\pi$  electrons) and the cyclopentadienyl radical (5  $\pi$  electrons) are unstable.
3. The cycloheptatrienyl cation.
  - a. Removal of  $H^+$  from cycloheptatriene produces the cycloheptatrienyl cation, which has 6  $\pi$  electrons and is stable.
  - b. The cycloheptatrienyl radical and anion are unstable.

### C. Aromatic heterocycles (Section 15.5).

1. A heterocycle (a cyclic compound containing one or more elements in addition to carbon) can also be aromatic.
2. Pyridine.
  - a. The nitrogen atom of pyridine contributes one  $\pi$  electron to the  $\pi$  system of the ring, making pyridine aromatic.
  - b. The nitrogen lone pair is not involved with the ring  $\pi$  system.
3. Pyrrole.
  - a. The nitrogen of pyrrole contributes both lone-pair electrons to the ring  $\pi$  system making pyrrole aromatic.
  - b. The nitrogen atom makes a different contribution to the  $\pi$  ring system in pyrrole and in pyridine.
4. Pyrimidine and imidazole rings are important in biological chemistry.

### D. Why $4n + 2$ ? (Section 15.6).

1. For aromatic compounds, there is a single lowest-energy MO that can accept two  $\pi$  electrons.
2. The next highest levels occur in degenerate pairs that can accept 4  $\pi$  electrons.
3. For all aromatic compounds and ions, a stable species occurs only when  $(4n + 2) \pi$  electrons are available to completely fill the bonding MOs.

## E. Polycyclic aromatic compounds (Section 15.7).

1. Although Hückel's Rule strictly applies only to monocyclic compounds, some polycyclic compounds show aromatic behavior.
2. Naphthalene has a Hückel number of  $\pi$  electrons and shows chemical and physical properties common to aromatic compounds.
3. There are many heterocyclic analogs of naphthalene.  
Tryptophan, adenine, and guanine are biologically important polycyclic aromatic compounds.

## IV. Spectroscopy of aromatic compounds (Section 15.8).

## A. IR spectroscopy.

1. A C–H stretch occurs at  $3030\text{ cm}^{-1}$ .
2. As many as 4 absorptions occur in the region  $1450\text{--}1600\text{ cm}^{-1}$ .
3. Weak absorptions are visible in the range  $1660\text{--}2000\text{ cm}^{-1}$ .
4. Strong absorptions in the region  $690\text{--}900\text{ cm}^{-1}$ , due to C–H out-of-plane bending, can be used to determine the substitution pattern of an aromatic ring.

## B. UV spectroscopy.

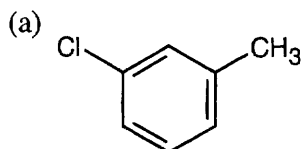
The conjugated  $\pi$  system of an aromatic ring gives rise to an intense absorption at 205 nm and weaker absorptions in the range 255–275 nm.

## C. NMR spectroscopy.

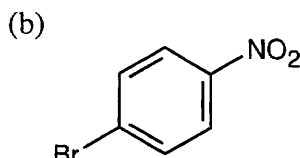
1.  $^1\text{H}$  NMR.
  - a. Hydrogens directly bonded to an aromatic ring absorb in the region 6.5–8.0  $\delta$ .
    - i. Spin–spin coupling can give information about the substitution pattern.
    - ii. Aromatic protons are deshielded because the applied magnetic field sets up a ring-current, which produces a small magnetic field that opposes the applied field and deshields the aromatic protons.
    - iii. If protons reside on the inside of an aromatic ring system, they are strongly shielded and absorb far upfield.
    - iv. The presence of a ring-current is a test of aromaticity.
  - b. Benzylic protons absorb at 2.3–3.0  $\delta$ .
2.  $^{13}\text{C}$  NMR.
  - a. Aromatic carbons absorb in the range 110–140  $\delta$ .
  - b. Since alkene carbons also absorb in this region,  $^{13}\text{C}$  NMR is not uniquely useful in identifying an aromatic ring.

## Solutions to Problems

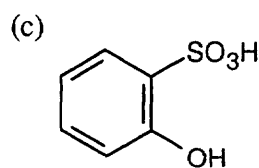
- 15.1** An ortho disubstituted benzene has two substituents in a 1,2 relationship. A meta disubstituted benzene has two substituents in a 1,3 relationship. A para disubstituted benzene has two substituents in a 1,4 relationship.



**meta disubstituted**

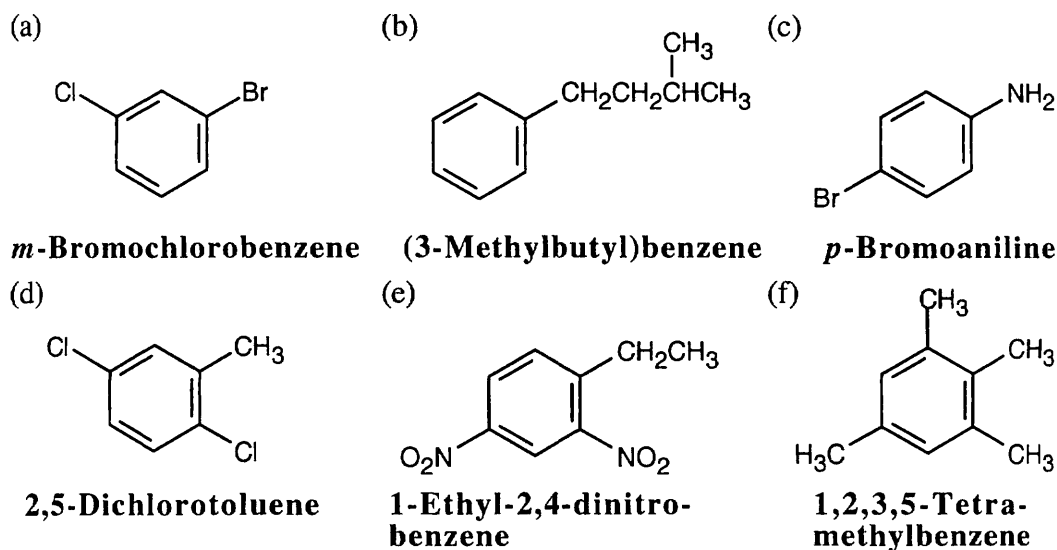


**para disubstituted**

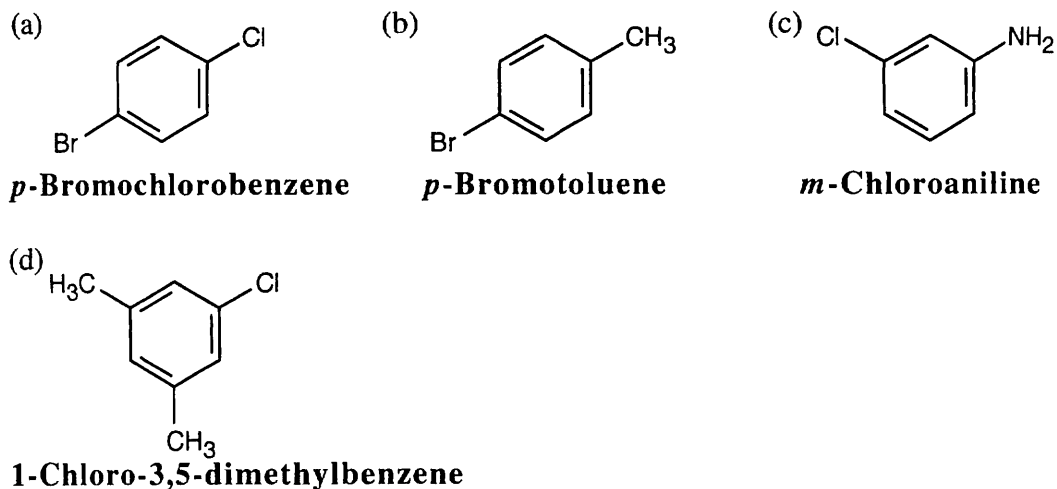


**ortho disubstituted**

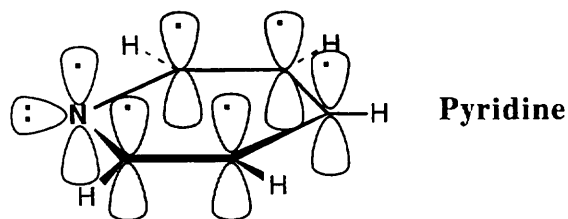
**15.2** Remember to give the lowest possible numbers to substituents on trisubstituted rings.



**15.3**

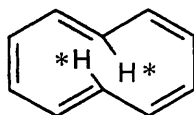


**15.4**



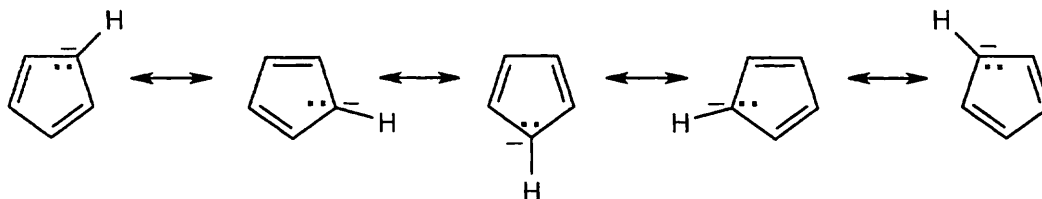
The electronic descriptions of pyridine and benzene are very similar. The pyridine ring is formed by the  $\sigma$  overlap of carbon and nitrogen  $sp^2$  orbitals. In addition, six  $p$  orbitals, perpendicular to the plane of the ring, hold six electrons. These six  $p$  orbitals form six  $\pi$  molecular orbitals that allow electrons to be delocalized over the  $\pi$  system of the pyridine ring. The lone pair of nitrogen electrons occupies an  $sp^2$  orbital that lies in the plane of the ring.

## 15.5



Cyclodecapentaene has  $4n + 2 \pi$  electrons ( $n = 2$ ), but it is not flat. If cyclodecapentaene were flat, the starred hydrogen atoms would crowd each other across the ring. To avoid this interaction, the molecule is distorted from planarity.

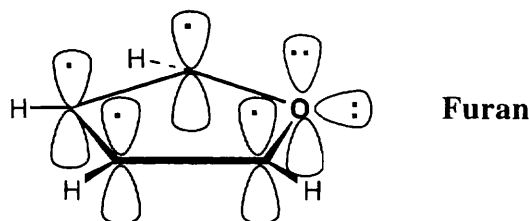
## 15.6



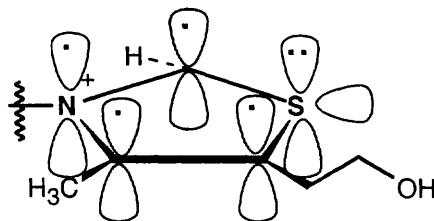
A compound that can be described by several resonance forms has a structure that can be represented by no one form. The structure of the cyclopentadienyl anion is a hybrid of all of the above structures and contains only one kind of carbon atom and one kind of hydrogen atom. All carbon–carbon bond lengths are equivalent, as are all carbon–hydrogen bonds lengths. Both the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra show only one absorption.

**15.7** When cyclooctatetraene accepts two electrons, it becomes a  $(4n + 2) \pi$  electron aromatic ion. Cyclooctatetraenyl dianion is planar with a carbon–carbon bond angle of  $135^\circ$  (a regular octagon).

**15.8** Furan is the oxygen analog of pyrrole. Furan is aromatic because it has  $6 \pi$  electrons in a cyclic, conjugated system. Oxygen contributes two lone-pair electrons from a  $p$  orbital perpendicular to the plane of the ring.

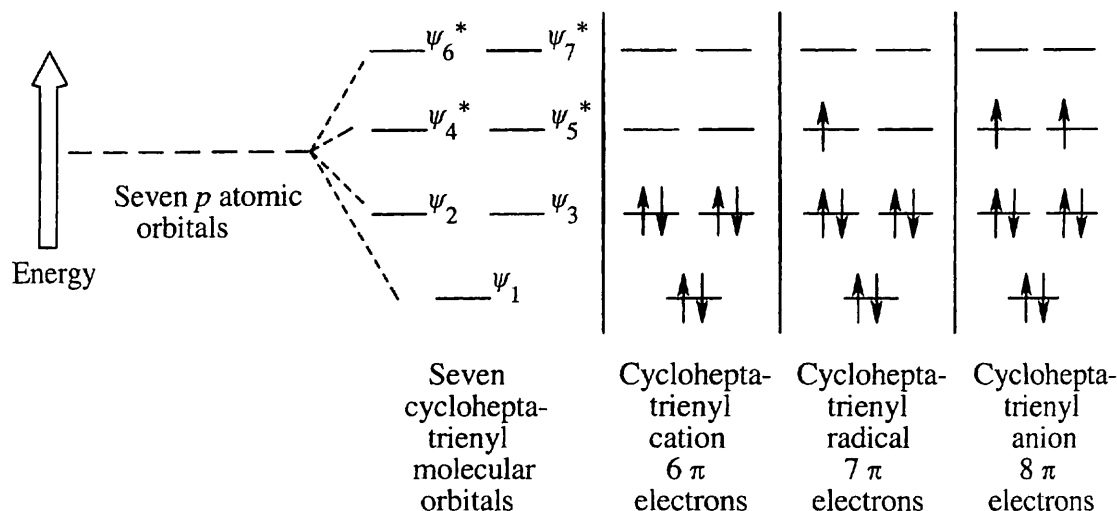


## 15.9



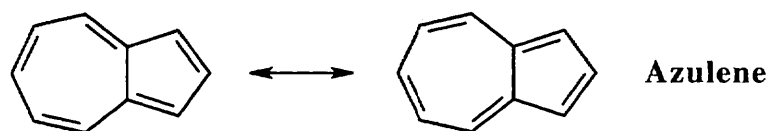
The heterocyclic thiazolium ring contains six  $\pi$  electrons. Each carbon contributes one electron, nitrogen contributes one electron, and sulfur contributes two electrons to the ring  $\pi$  system. The thiazolium ion is aromatic because it has  $6 \pi$  electrons in a cyclic, conjugated system.

## 15.10



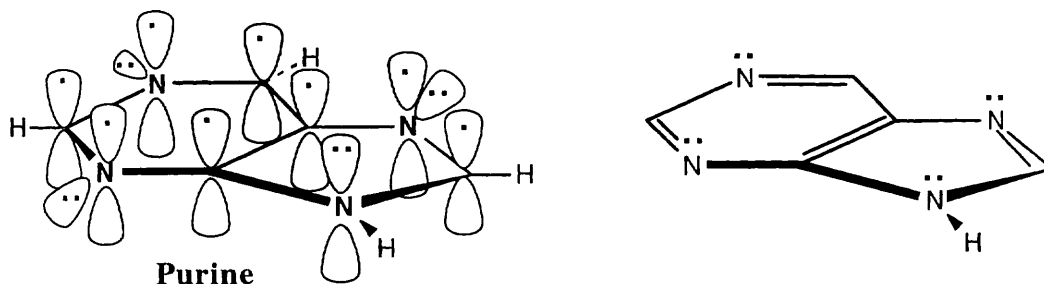
The cycloheptatrienyl cation has six  $\pi$  electrons (a Hückel number) and is aromatic.

## 15.11



Azulene is aromatic because it has a conjugated cyclic  $\pi$  electron system containing ten  $\pi$  electrons (a Hückel number).

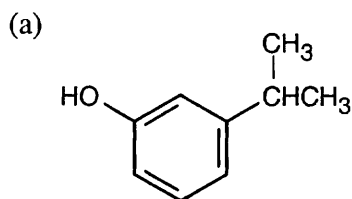
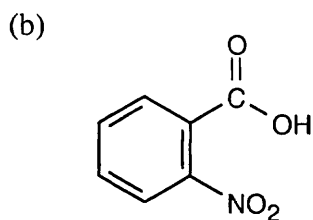
## 15.12



Purine is a ten- $\pi$ -electron aromatic molecule. The N–H nitrogen atom in the five-membered ring donates both electrons of its lone pair to the  $\pi$  electron system, and each of the other three nitrogens donates one electron to the  $\pi$  electron system.

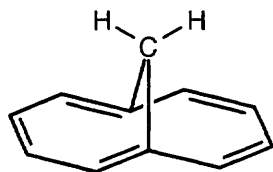
## Visualizing Chemistry

## 15.13

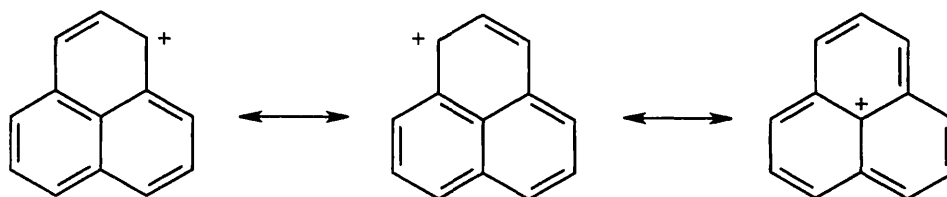
***m*-Isopropylphenol*****o*-Nitrobenzoic acid**

**15.14** The all-cis cyclodecapentaene shown here is not aromatic because it is not planar. All hydrogens, however, are equivalent and show one absorption in the vinylic region of the molecule's  $^1\text{H}$  NMR spectrum. If the molecule were planar and therefore aromatic, the absorption would appear between 6.5–8.0  $\delta$ .

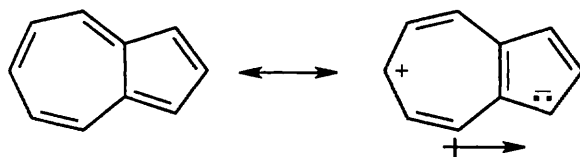
**15.15** 1,6-Methanonaphthalene has ten  $\pi$  electrons and is sufficiently planar to behave as an aromatic molecule. The perimeter hydrogens absorb in the aromatic region of the  $^1\text{H}$  NMR spectrum (6.9–7.3  $\delta$ ). Interaction of the applied magnetic field with the perimeter  $\pi$  electrons sets up a ring current (see Section 15.8) that strongly shields the  $\text{CH}_2$  protons and causes them to absorb far upfield (–0.5  $\delta$ ).



**15.16** Three resonance forms for the carbocation of the formula  $\text{C}_{13}\text{H}_9$  are shown below, and more can be drawn. These forms show that the positive charge of the carbocation can be stabilized in the same way as an allylic or benzylic carbocation is stabilized – by overlap with the neighboring  $\pi$  electrons of the ring system.



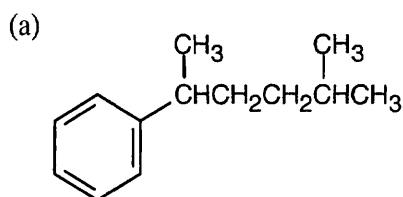
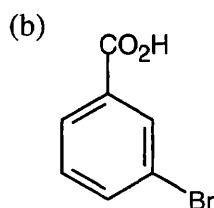
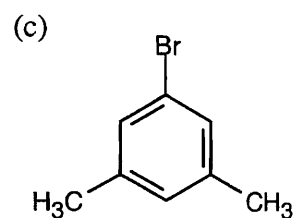
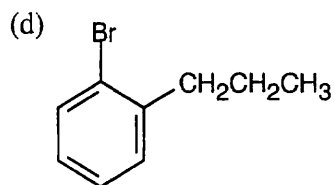
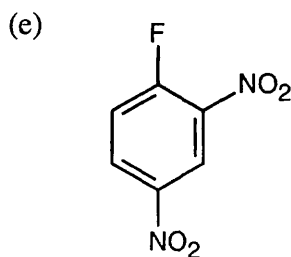
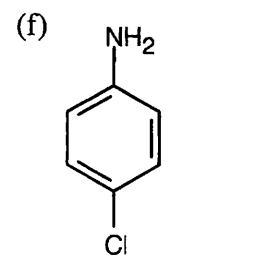
## 15.17



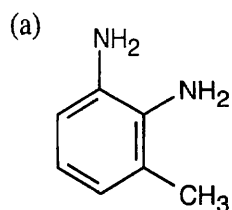
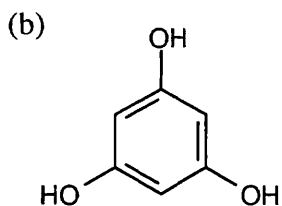
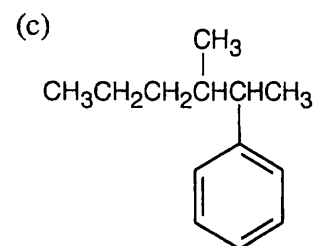
Molecules with dipole moments are polar because electron density is drawn from one part of the molecule to another. In azulene, electron density is drawn from the seven-membered ring to the five-membered ring, satisfying Hückel's rule for both rings and producing a dipole moment. The five-membered ring resembles the cyclopentadienyl anion in having six  $\pi$  electrons, while the seven-membered ring resembles the cycloheptatrienyl cation. The electrostatic potential map shows that the five-membered ring is more electron-rich than the seven-membered ring.

## Additional Problems

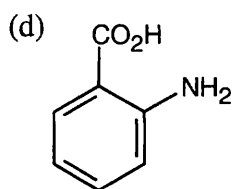
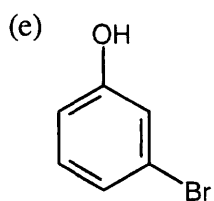
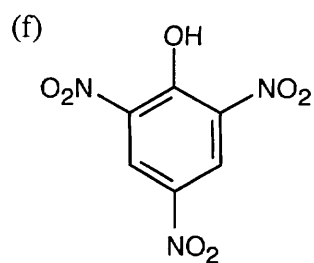
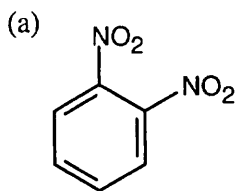
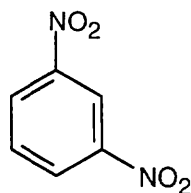
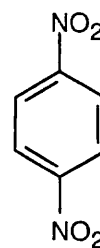
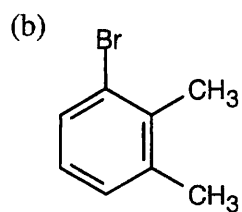
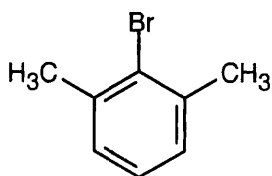
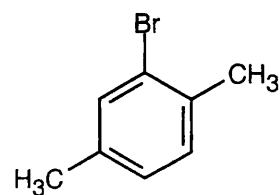
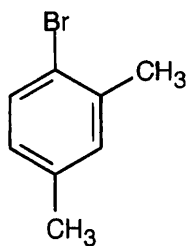
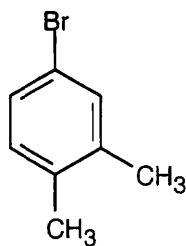
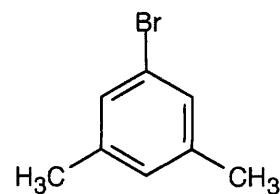
## 15.18

**2-Methyl-5-phenylhexane*****m*-Bromobenzoic acid****1-Bromo-3,5-dimethylbenzene*****o*-Bromopropylbenzene****1-Fluoro-2,4-dinitrobenzene*****p*-Chloroaniline**

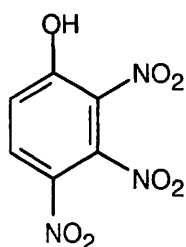
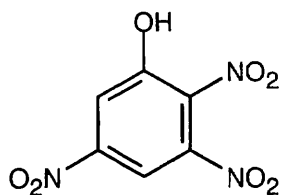
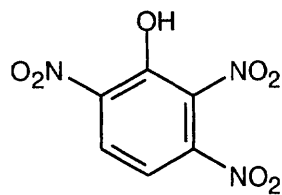
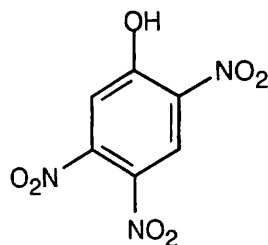
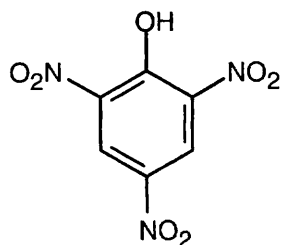
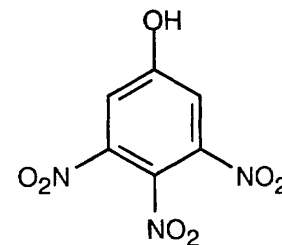
## 15.19

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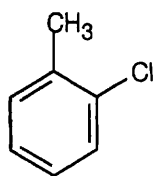
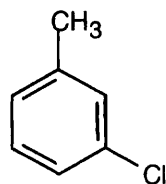
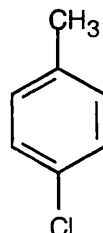
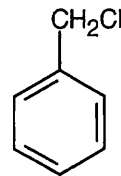


***o*-Aminobenzoic acid*****m*-Bromophenol****2,4,6-Trinitrophenol****15.20*****o*-Dinitrobenzene*****m*-Dinitrobenzene*****p*-Dinitrobenzene****1-Bromo-2,3-dimethylbenzene****2-Bromo-1,3-dimethylbenzene****2-Bromo-1,4-dimethylbenzene****1-Bromo-2,4-dimethylbenzene****4-Bromo-1,2-dimethylbenzene****1-Bromo-3,5-dimethylbenzene**

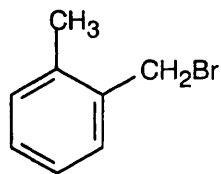
(c)

**2,3,4-Trinitrophenol****2,3,5-Trinitrophenol****2,3,6-Trinitrophenol****2,4,5-Trinitrophenol****2,4,6-Trinitrophenol****3,4,5-Trinitrophenol**

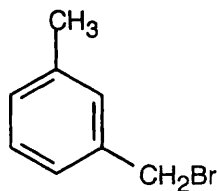
**15.21** All aromatic compounds of formula  $C_7H_7Cl$  have one ring and three double bonds.

***o*-Chlorotoluene*****m*-Chlorotoluene*****p*-Chlorotoluene****Benzyl chloride  
(Chloromethyl)-  
benzene**

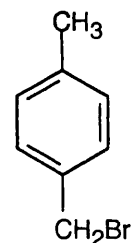
**15.22** Six of these compounds are illustrated and named in Problem 15.20(b). The other eight are:



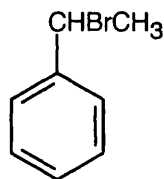
***o*-(Bromomethyl)-toluene**



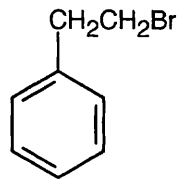
***m*-(Bromomethyl)-toluene**



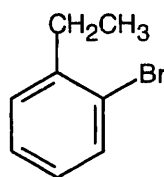
***p*-(Bromomethyl)-toluene**



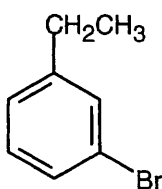
**(1-Bromoethyl)benzene**



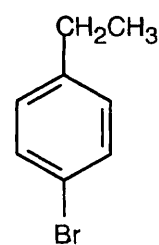
**(2-Bromoethyl)benzene**



***o*-Bromoethylbenzene**



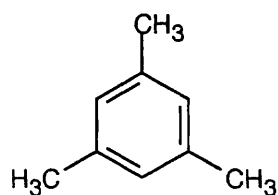
***m*-Bromoethylbenzene**



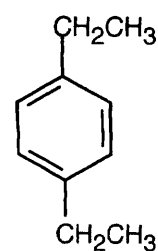
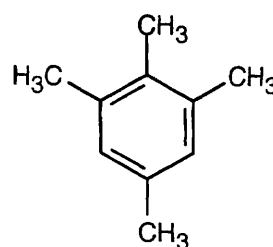
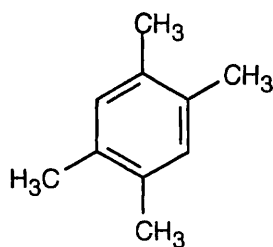
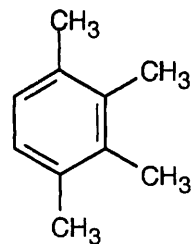
***p*-Bromoethylbenzene**

**15.23** All compounds in this problem have four double bonds and/or rings and must be substituted benzenes, if they are to be aromatic. They may be substituted by methyl, ethyl, propyl, or butyl groups.

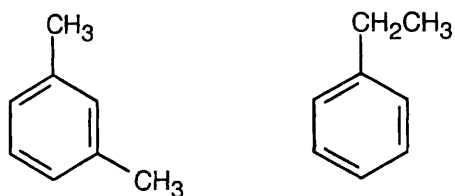
(a)



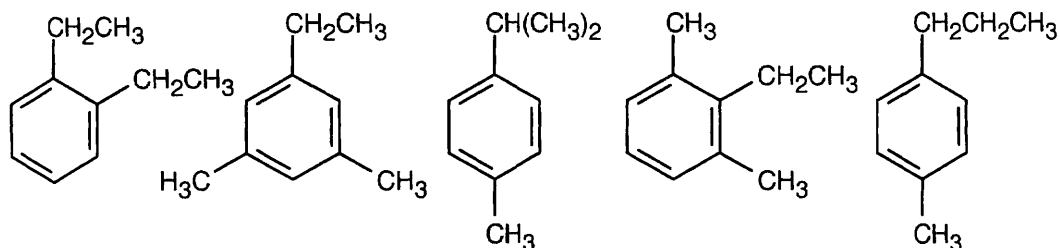
(b)



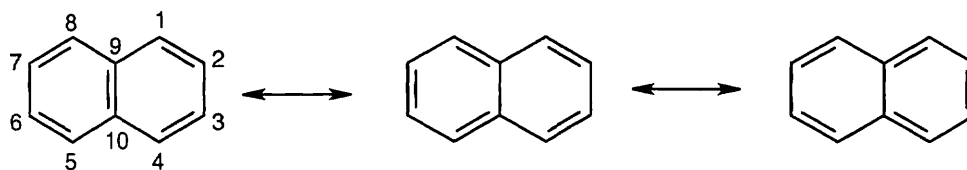
(c)



(d)

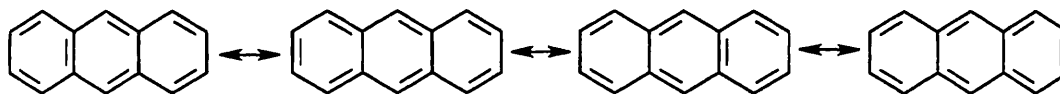


## 15.24

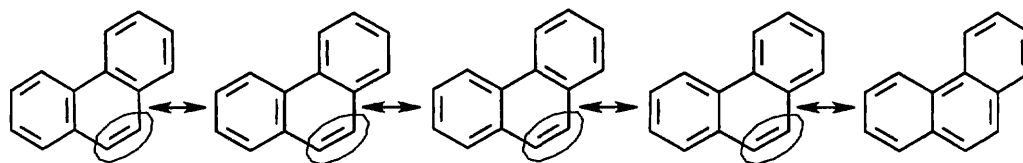


The bond between carbons 1 and 2 is represented as a double bond in two of the three resonance structures, but the bond between carbons 2 and 3 is represented as a double bond in only one resonance structure. The C1–C2 bond thus has more double-bond character in the resonance hybrid, and it is shorter than the C2–C3 bond. The C3–C4, C5–C6, and C7–C8 bonds also have more double-bond character than the remaining bonds.

## 15.25

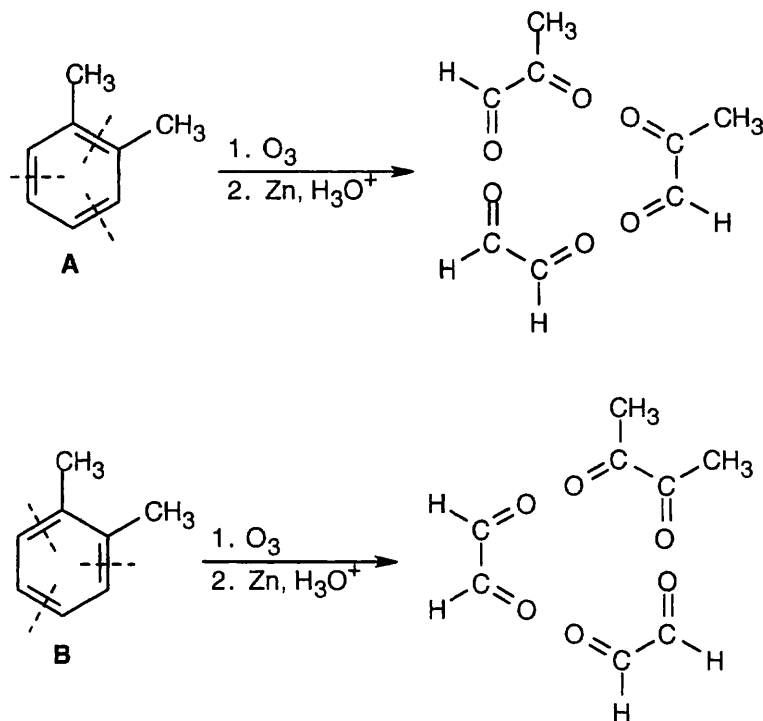


## 15.26, 15.27



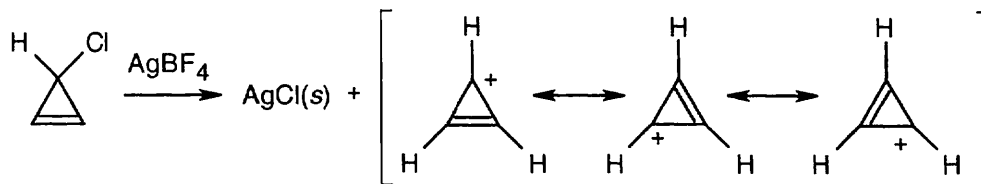
The circled bond is represented as a double bond in four of the five resonance forms of phenanthrene. This bond has more double-bond character and thus is shorter than the other carbon–carbon bonds of phenanthrene.

## 15.28



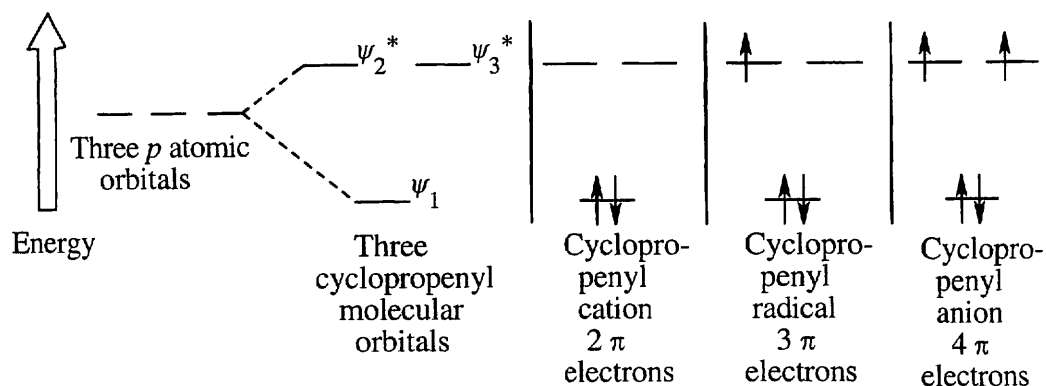
If *o*-xylene exists only as structure **A**, ozonolysis would cause cleavage at the bonds indicated and would yield two equivalents of pyruvaldehyde and one equivalent of glyoxal for each equivalent of **A** consumed. If *o*-xylene exists only as structure **B**, ozonolysis would yield one equivalent of 2,3-butanedione and two equivalents of glyoxal. If *o*-xylene exists as a resonance hybrid of **A** and **B**, the ratio of ozonolysis products would be glyoxal : pyruvaldehyde : 2,3-butanedione = 3:2:1. Since this ratio is identical to the experimentally determined ratio, we know that **A** and **B** contribute equally to the structure of *o*-xylene. Note that these data don't distinguish between the resonance hybrid structure and the alternate possibility, equilibrium between two isomeric *o*-xylenes.

## 15.29



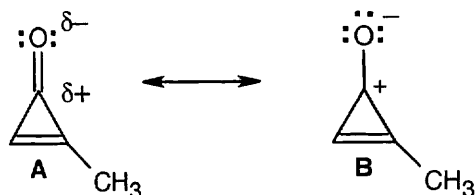
The product of the reaction of 3-chlorocyclopropene with  $\text{AgBF}_4$  is the cyclopropenyl cation  $\text{C}_3\text{H}_3^+$ . The resonance structures of the cation indicate that all hydrogen atoms are equivalent, and the  $^1\text{H}$  NMR spectrum, which shows only one type of hydrogen atom, confirms this equivalence. The cyclopropenyl cation contains two  $\pi$  electrons and is aromatic according to Hückel's rule. (Here,  $n = 0$ .)

## 15.30



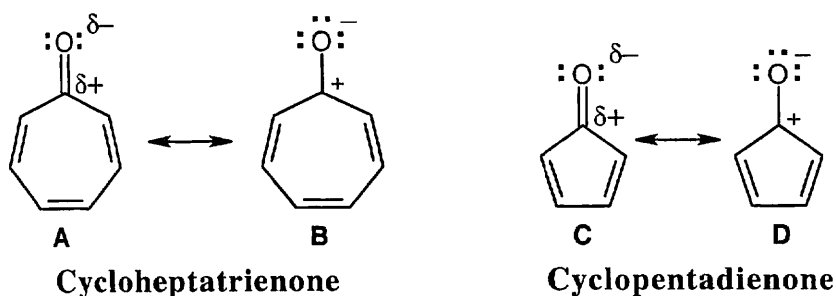
The cyclopropenyl cation is aromatic, according to Hückel's rule.

## 15.31



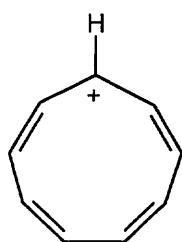
In resonance structure **A**, methylcyclopropenone is a cyclic conjugated compound with three  $\pi$  electrons in its ring. Because the electronegative oxygen attracts the  $\pi$  electrons of the carbon–oxygen  $\pi$  bond, however, a second resonance structure **B** can be drawn in which both carbonyl  $\pi$  electrons are located on oxygen, leaving only two  $\pi$  electrons in the ring. Since 2 is a Hückel number, the methylcyclopropenone ring is aromatic and is expected to be stable.

## 15.32

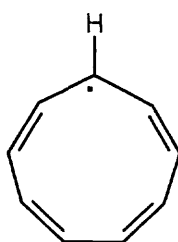


As in the previous problem, we can draw resonance forms in which both carbonyl  $\pi$  electrons are located on oxygen. The cycloheptatrienone ring in **B** contains six  $\pi$  electrons and is aromatic according to Hückel's rule. The cyclopentadienone ring in **D** contains four  $\pi$  electrons and is antiaromatic.

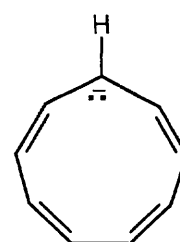
**15.33** Check the number of electrons in the  $\pi$  system of each compound. The species with a Hückel ( $4n + 2$ ) number of  $\pi$  electrons is the most stable.



cation  
8  $\pi$  electrons



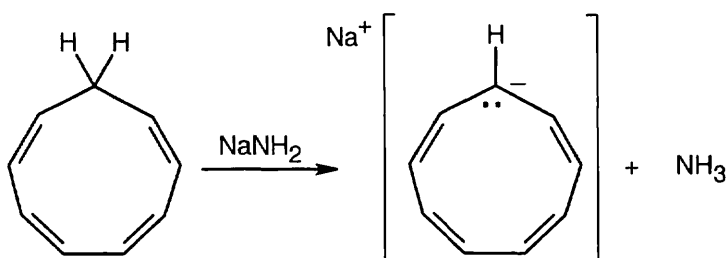
radical  
9  $\pi$  electrons



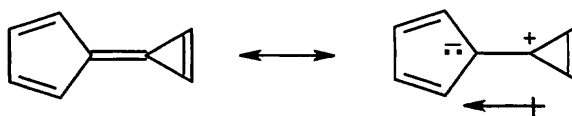
anion  
10  $\pi$  electrons

The 10  $\pi$  electron anion is the most stable.

**15.34** Treat 1,3,5,7-cyclononatetraene with a strong base to remove a proton.

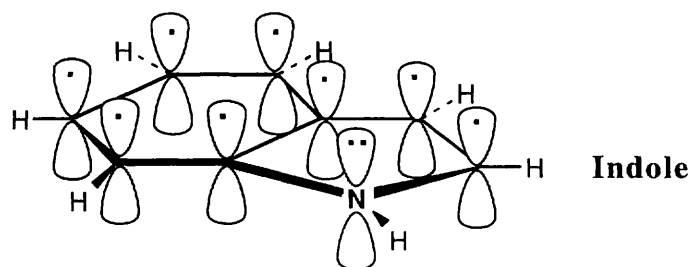


**15.35** As with azulene, redistribution of the  $\pi$  electrons of calicene produces a resonance form in which both rings are aromatic and which has a dipole moment.



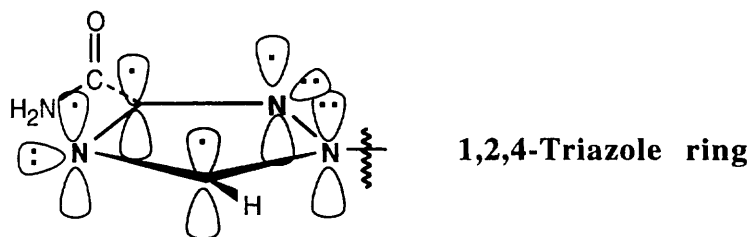
**15.36** Pentalene has eight  $\pi$  electrons and is antiaromatic. Pentalene dianion, however, has ten  $\pi$  electrons and is a stable, aromatic ion.

**15.37**

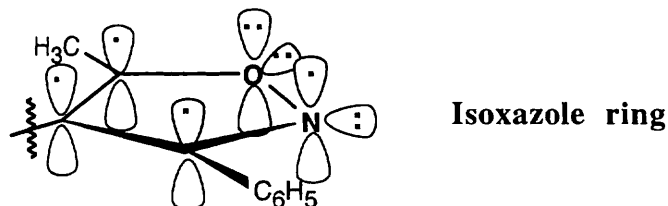


Indole, like naphthalene, has ten  $\pi$  electrons in two rings and is aromatic. Two  $\pi$  electrons come from the nitrogen atom.

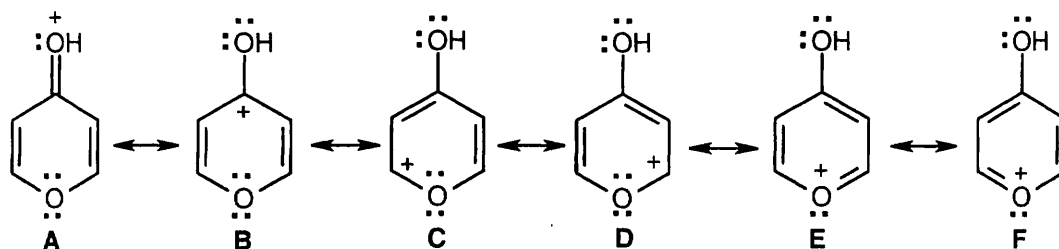
**15.38** The 1,2,4-triazole ring is aromatic because it has 6  $\pi$  electrons in a cyclic, conjugated system.



**15.39** The isoxazole ring is aromatic for the same reasons as the 1,2,4-triazole ring is aromatic.

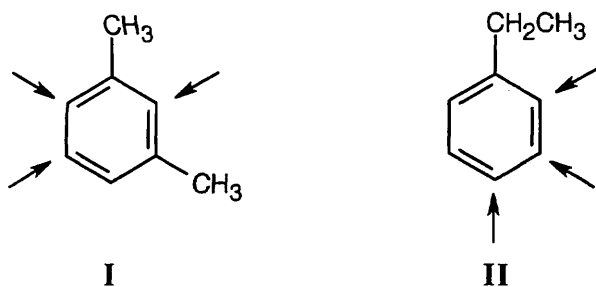


**15.40**



Protonation of 4-pyrone gives structure **A**, which has resonance forms **B**, **C**, **D**, **E** and **F**. In **E** and **F**, a lone pair of electrons of the ring oxygen is delocalized into the ring to produce a six  $\pi$  electron system, which should be aromatic according to Hückel's rule.

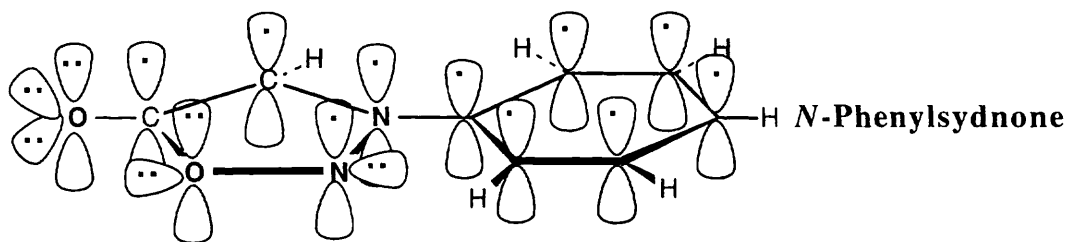
**15.41** Compound **A** has four multiple bonds and/or rings. Possible structures that yield three monobromo substitution products are:



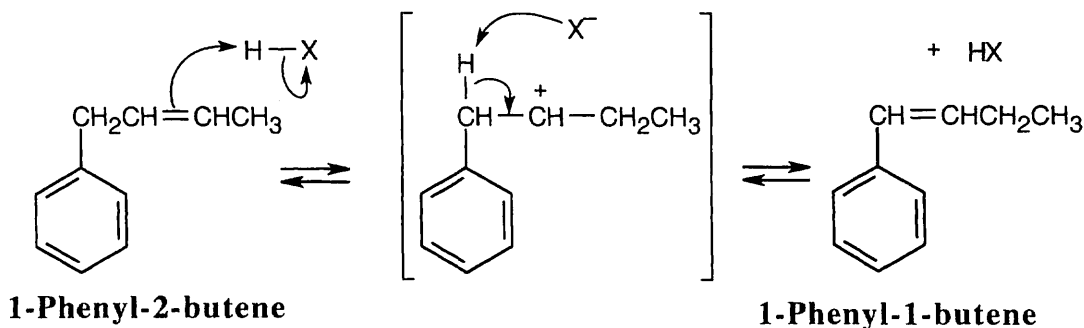
Only structure **I** shows a six-proton singlet at 2.30  $\delta$ , because it contains two identical benzylic methyl groups unsplit by other protons. The presence of four protons in the aromatic region of the  $^1\text{H}$  NMR spectrum confirms that **I** is the correct structure.



- 15.42** The second resonance form of *N*-phenylsydnone shows the aromaticity of the five-membered ring more clearly. In this form, the ring oxygen contributes two electrons to the ring  $\pi$  system, each nitrogen contributes one electron and each carbon contributes one electron (the carbonyl oxygen bears a formal negative charge). This 6  $\pi$  electron, cyclic conjugated system obeys Hückel's rule.

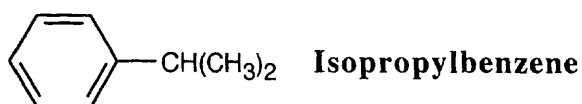


**15.43**



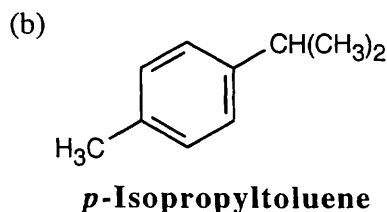
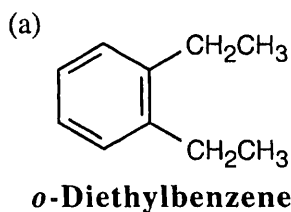
The alkene double bond is protonated to yield an intermediate carbocation, which loses a proton to give a product in which the double bond is conjugated with the aromatic ring, as shown by the increased value of  $\lambda_{\text{max}}$ .

- 15.44** The molecular weight of the hydrocarbon (120) corresponds to the molecular formula  $\text{C}_9\text{H}_{12}$ , which indicates four double bonds and/or rings. The  $^1\text{H}$  NMR singlet at 7.25  $\delta$  indicates five aromatic ring protons. The septet at 2.90  $\delta$  is due to a benzylic proton that has six neighboring protons.

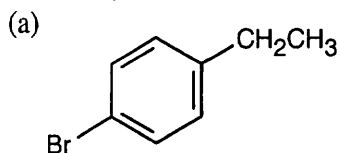
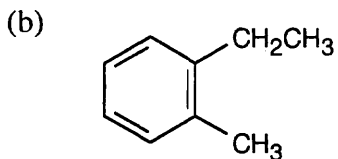
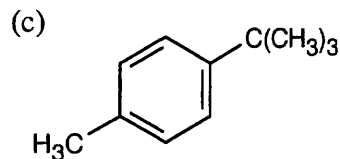


- 15.45** Both hydrocarbons are disubstituted benzenes. The compound in (a) has two ethyl groups, and the compound in (b) has an isopropyl group and a methyl group. The IR data must be used to find the pattern of substitution.

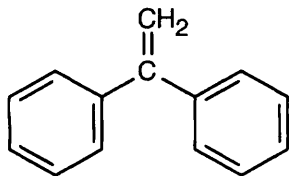
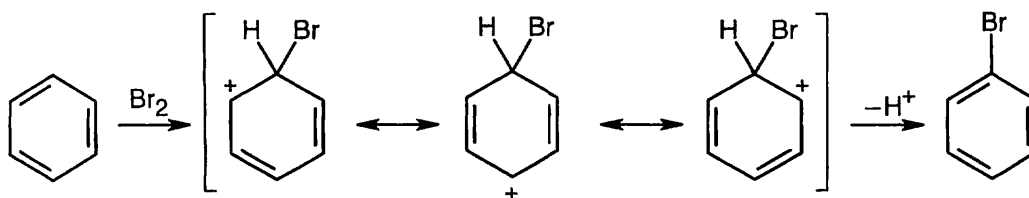
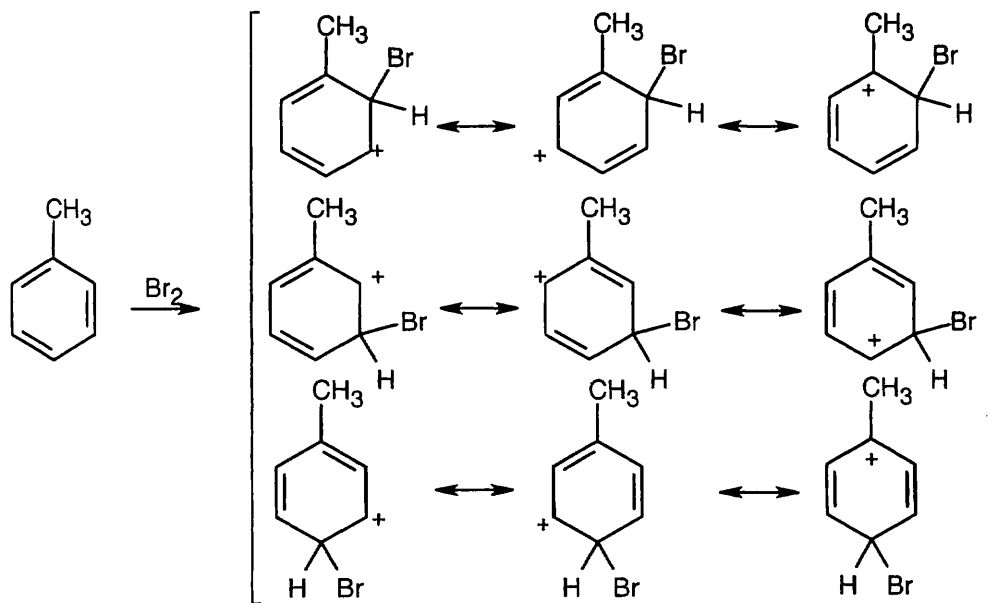
Data in Section 15.8 show that an IR absorption of  $745\text{ cm}^{-1}$  corresponds to an *o*-disubstituted benzene, and an absorption of  $825\text{ cm}^{-1}$  corresponds to a *p*-disubstituted benzene.



- 15.46** All of these compounds have 4 degrees of unsaturation and are substituted benzenes. The benzylic absorptions (2.3–3.0  $\delta$ ) identify the hydrogens next to the aromatic ring. Remember that the data from the IR spectrum can be used to assign the substitution pattern of the ring.

***p*-Bromoethylbenzene*****o*-Ethyltoluene*****p*-tert-Butyltoluene**

- 15.47** The compound has nine degrees of unsaturation. The  $^1\text{H}$  NMR spectrum shows that the compound is symmetrical and that the only absorptions occur in the vinylic and aromatic regions of the spectrum. The IR spectrum shows peaks due to a monosubstituted benzene ring and to  $\text{R}_2\text{C}=\text{CH}_2$  ( $890\text{ cm}^{-1}$ ).

**15.48****15.49**

The ortho and para products predominate because the intermediate carbocation is more stabilized. The third resonance form drawn for ortho-para attack places the positive charge at the methyl-substituted carbon, which is a more stable tertiary carbocation.