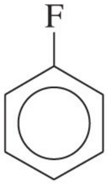
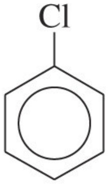
# Chapter 14
# Aromatic Compounds

# ♦ Nomenclature of Benzene Derivatives

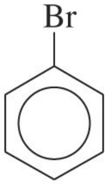
- ➔ **Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix**



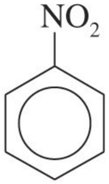
**Fluorobenzene**



**Chlorobenzene**

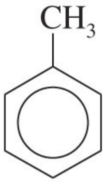


**Bromobenzene**

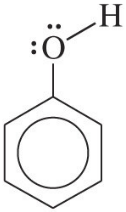


**Nitrobenzene**

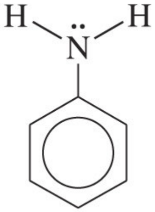
- ➔ **For other monosubstituted benzenes, the presence of the substituent results in a new parent name**



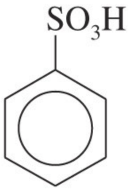
**Toluene**



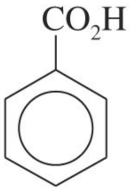
**Phenol**



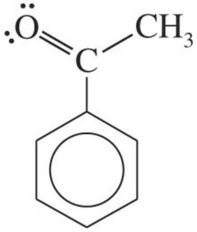
**Aniline**



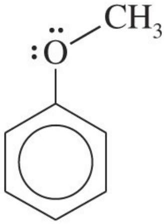
**Benzenesulfonic acid**



**Benzoic acid**

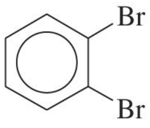


**Acetophenone**

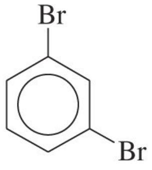


**Anisole**

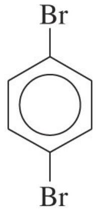
➔ **When two substituents are present their position may be indicated by the prefixes *ortho*, *meta,* and *para* (*o*, *m* and *p*) or by the corresponding numerical positions**



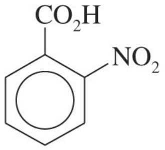
**1,2-Dibromobenzene**
**(*o*-dibromobenzene)**
**ortho**



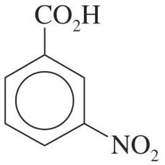
**1,3-Dibromobenzene**
**(*m*-dibromobenzene)**
**meta**



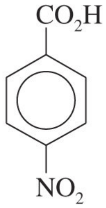
**1,4-Dibromobenzene**
**(*p*-dibromobenzene)**
**para**



**2-Nitrobenzoic acid**
**(*o*-nitrobenzoic acid)**



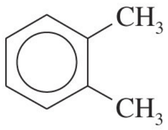
**3-Nitrobenzoic acid**
**(*m*-nitrobenzoic acid)**



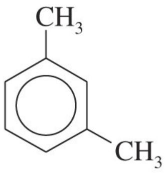
**4-Nitrobenzoic acid**
**(*p*-nitrobenzoic acid)**

$CH_3$ $CH_3$

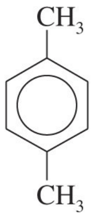
➔ **Dimethyl substituted benzenes are called xylenes**



**1,2-Dimethylbenzene**
**(*o*-xylene)**



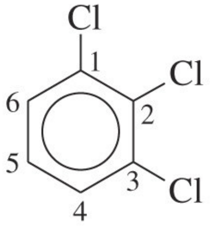
**1,3-Dimethylbenzene**
**(*m*-xylene)**



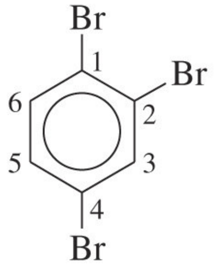
**1,4-Dimethylbenzene**
**(*p*-xylene)**

➔ **Numbers must be used as locants when more than two substituents are present**

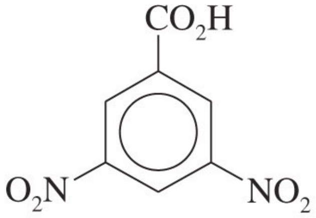
- **The lowest possible set of numbers should be given to the substituents**
- **The substituents should be listed in alphabetical order**
- **If one of the substituents defines a parent other than benzene, this substituent defines the parent name and should be designated position 1**



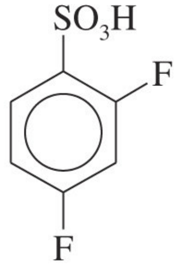
**1,2,3-Trichlorobenzene**



**1,2,4-Tribromobenzene**
**(*not* 1,3,4-tribromobenzene)**



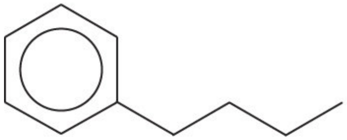
**3,5-Dinitrobenzoic acid**



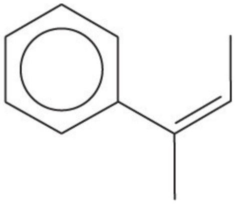
**2,4-Difluorobenzenesulfonic acid**

**➔The $C_6H_5$- group is called phenyl when it is a substituent**

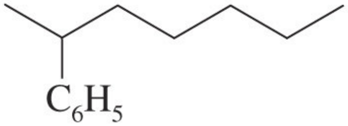
- **Phenyl is abbreviated Ph or Φ**
- **A hydrocarbon with a saturated chain and a benzene ring is named by choosing the larger structural unit as the parent**
- **If the chain is unsaturated then it must be the parent and the benzene is then a phenyl substituent**



Butylbenzene

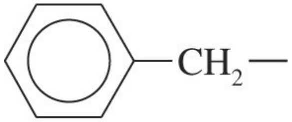


(*Z*)-2-Phenyl-2-butene

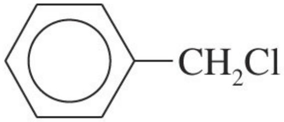


2-Phenylheptane

**➔The phenylmethyl group is called a benyl (abbreviated Bz)**



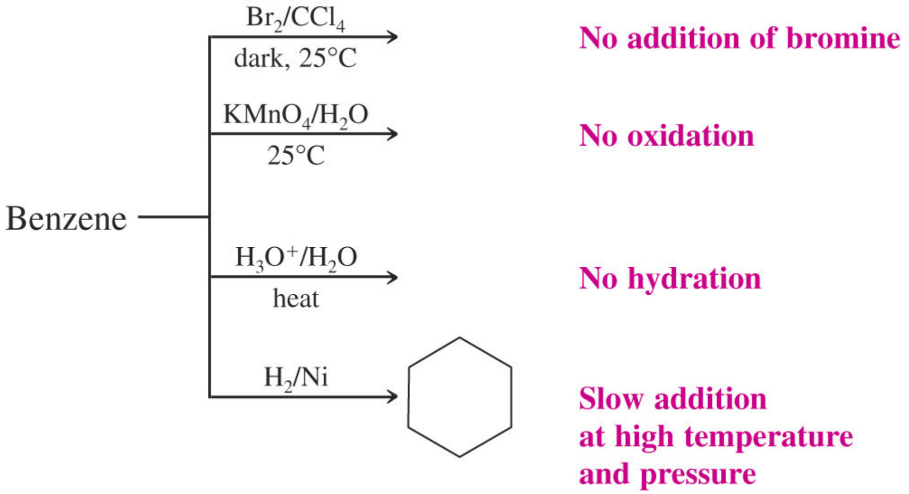
The benzyl group (the phenylmethyl group)



Benzyl chloride (phenylmethyl chloride or BzCl)

# ♦ Reactions of Benzene

➔ **Even though benzene is highly unsaturated it does not undergo any of the regular reactions of alkenes such as addition or oxidation**



➔ **Benzene can be induced to react with bromine if a Lewis acid catalyst is present however the reaction is a *substitution* and not an addition**

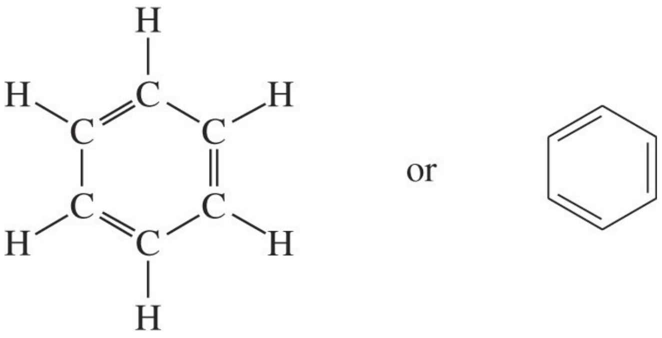
- **Benzene produces only one monobrominated compound, which indicates that all 6 carbon-hydrogen bonds are equivalent in benzene**

$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$ **Observed**

$C_6H_6 + Br_2 \not\longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6$ **Not observed**

# ♦ The Kekule Structure for Benzene

- ➔ **Kekule was the first to formulate a reasonable representation of benzene**



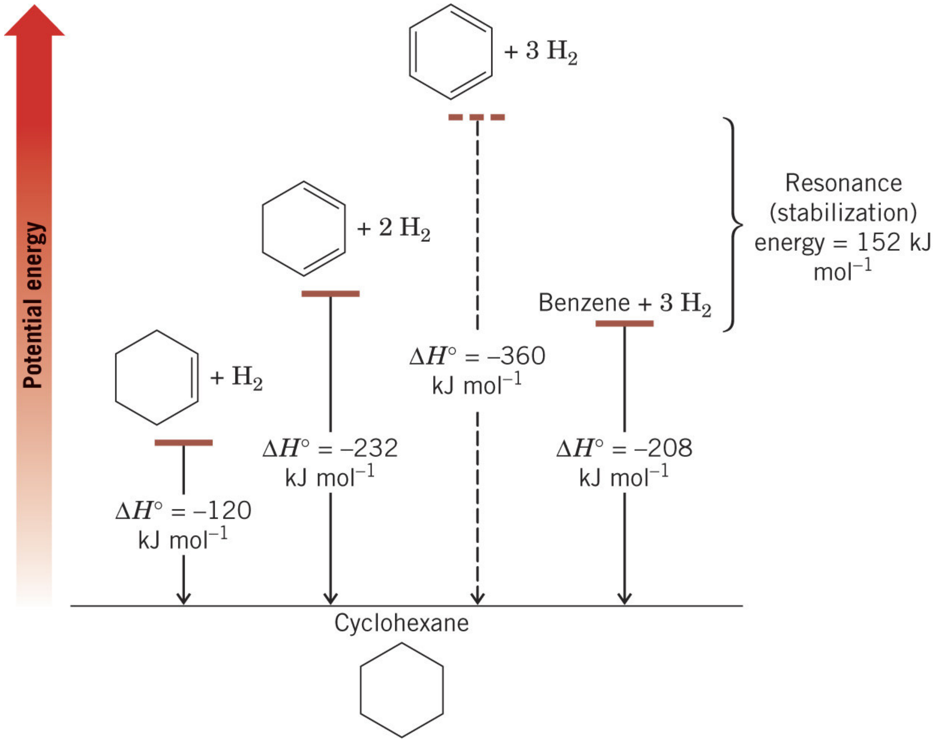
The Kekulé formula for benzene

- ➔ **The Kekule structure suggests alternating double and single carbon-carbon bonds**
  - **Based on the Kekule structure one would expect there to be two different 1,2-dibromobenzenes but there is only one**
  - **Kekule suggested an equilibrium between these compounds to explain this observation but it is now known no such equilibrium exists**

# ♦ The Stability of Benzene

➔ **Benzene is much more stable than would be expected based on calculations for "cyclohexatriene"**

- **A reasonable prediction for the heat of hydrogenation of hypothetical cyclohexatriene is -360 kJ mol$^{-1}$ (3 times that of cyclohexene, -120 kJ mol$^{-1}$ )**
- **The experimentally determined heat of hydrogenation for benzene is -280 mol$^{-1}$, 152 kJ mol$^{-1}$ more stable than hypothetical cyclohexatriene**
- **This difference is called the resonance energy**

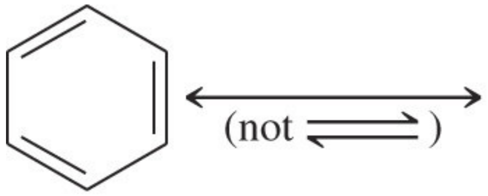


# ♦ Modern Theories of the Structure of Benzene

## ● The Resonance Explanation of the Structure of Benzene

➔ Structures I and II are equal resonance contributors to the real structure of benzene

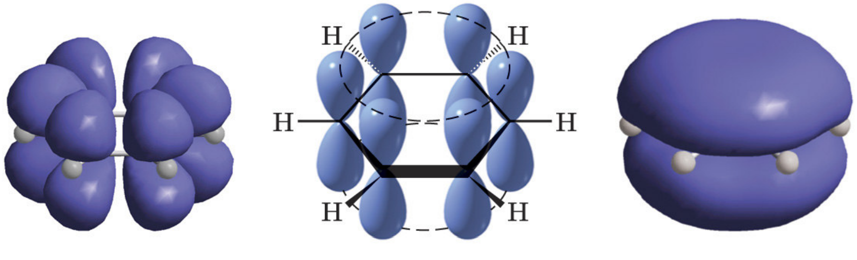
- Benzene is particularly stable because it has two equivalent and important resonance structures
- Each carbon-carbon bond is 1.39 Å, which is between the length of a carbon-carbon single bond between *sp*$^2$ carbons (1.47Å) and a carbon-carbon double bond (1.33 Å)
- Often the hybrid is represented by a circle in a hexagon (III)



**I** **II**

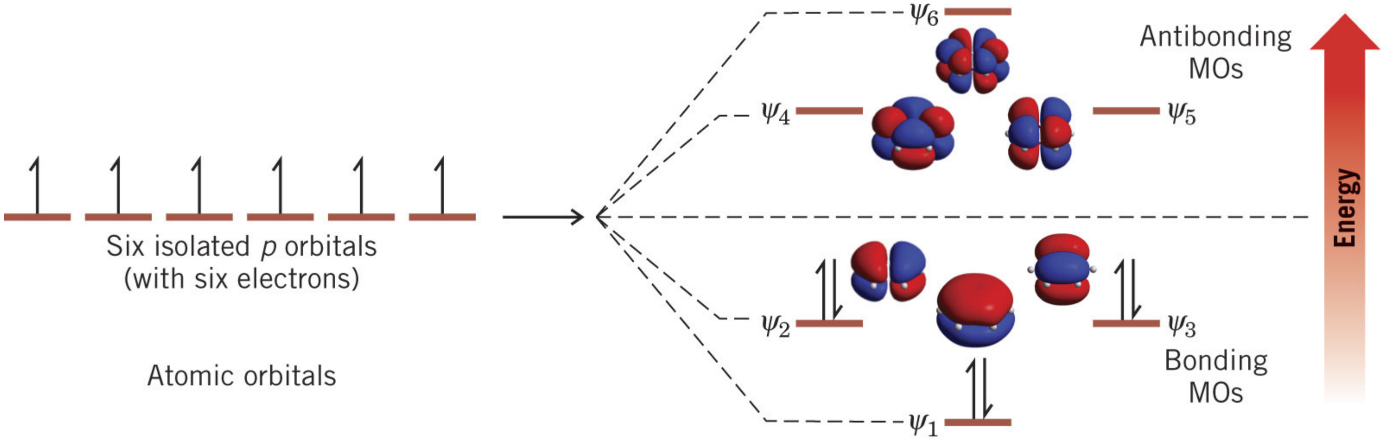
**III**

- **The Molecular Orbital Explanation of the Structure of Benzene**
  - **The carbons in benzene are *sp*$^2$ hybridized with *p* orbitals on all 6 carbons (a)**
    - **The *p* orbitals overlap around the ring (b) to form a bonding molecular orbital with electron density above and below the plane of the ring (c)**



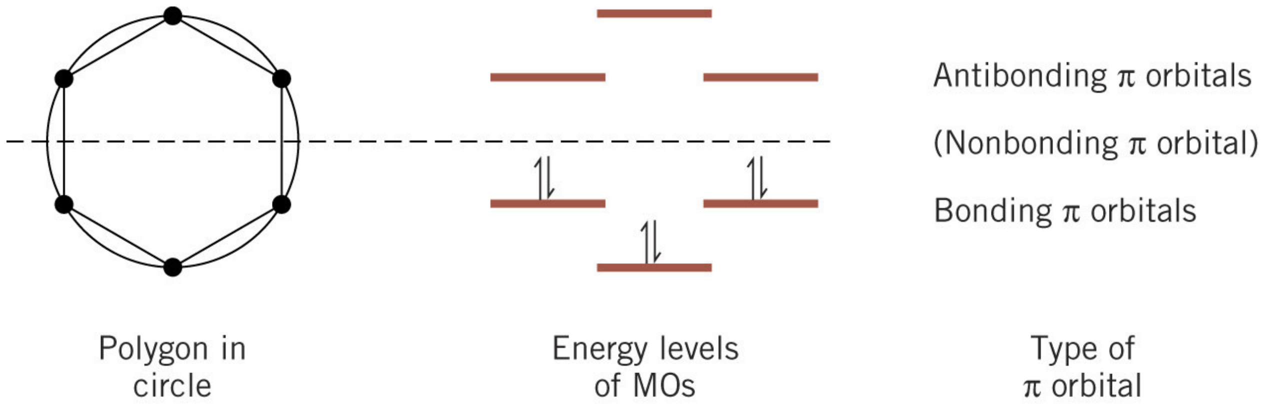
(*a*) (*b*) (*c*)

  - **There are six π molecular orbitals for benzene**

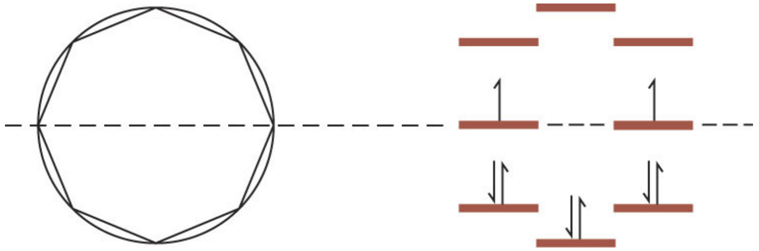


# ♦ Huckel's Rule: The 4n+2π Electron Rule

- ➔ **Planar monocyclic rings with a continuous system of *p* orbitals and 4n + 2π electrons are aromatic (n = 0, 1, 2, 3 etc)**
  - **Aromatic compounds have substantial resonance stabilization**
  - **Benzene is aromatic: it is planar, cyclic, has a *p* orbital at every carbon, and 6 π electrons (n=1)**
- ➔ **There is a *polygon-and-circle method* for deriving the relative energies of orbitals of a system with a cyclic continuous array of *p* orbitals**
  - **A polygon corresponding to the ring is inscribed in a circle with one point of the polygon pointing directly down**
  - **A horizontal line is drawn where vertices of the polygon touch the circle - each line corresponds to the energy level of the π MOs at those atoms**
  - **A dashed horizontal line half way up the circle indicates the separation of bonding and antibonding orbitals**
- ➔ **Benzene has 3 bonding and 3 antibonding orbitals**
  - **All the bonding orbitals are full and there are no electrons in antibonding orbitals; benzene has a closed shell of delocalized electrons and is very stable**

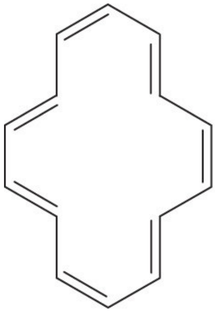


- ➔ **Cyclooctatetraene has two nonbonding orbitals each with one electron**
  - **This is an unstable configuration; cyclooctatetraene adopts a nonplanar conformation with localized π bonds to avoid this instability**

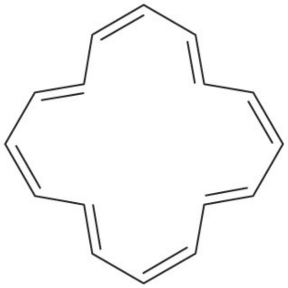


## The Annulenes

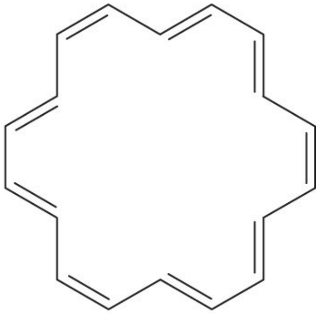
- **Annulenes are monocyclic compounds with alternating double and single bonds**
    - **Annulenes are named using a number in brackets that indicates the ring size**
    - **Benzene is [6]annulene and cyclooctatetraene is [8]annulene**
    - **An annulene is aromatic if it has 4n+2π electrons and a planar carbon skeleton**
- **The [14]and [18]annulenes are aromatic (4n+2, where n= 3,4)**
    - **The [16] annulene is not aromatic**



**[14]Annulene**
**(aromatic)**

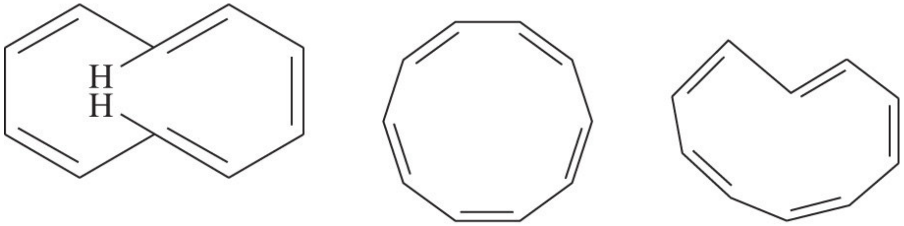


**[16]Annulene**
**(*not* aromatic)**



**[18]Annulene**
**(aromatic)**

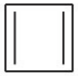
- **The [10]annulenes below should be aromatic but none of them can be planar**
  - **4 is not planar because of steric interaction of the indicated hydrogens**
  - **5 and 6 are not be planar because of large angle strain in the flat molecules**



**4** **5** **6**

**[10]Annulenes**
**None is aromatic because none is planar.**

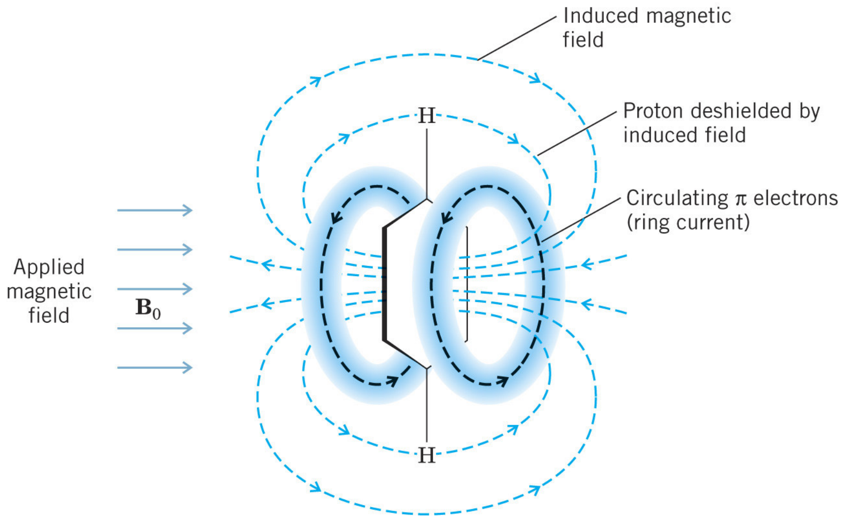
- **Cyclobutadiene is a [4]annulene and is not aromatic**
  - **It does not follow the 4n+ 2 rule and is highly unstable**



**Cyclobutadiene**
**or [4]annulene**
**(*not* aromatic)**

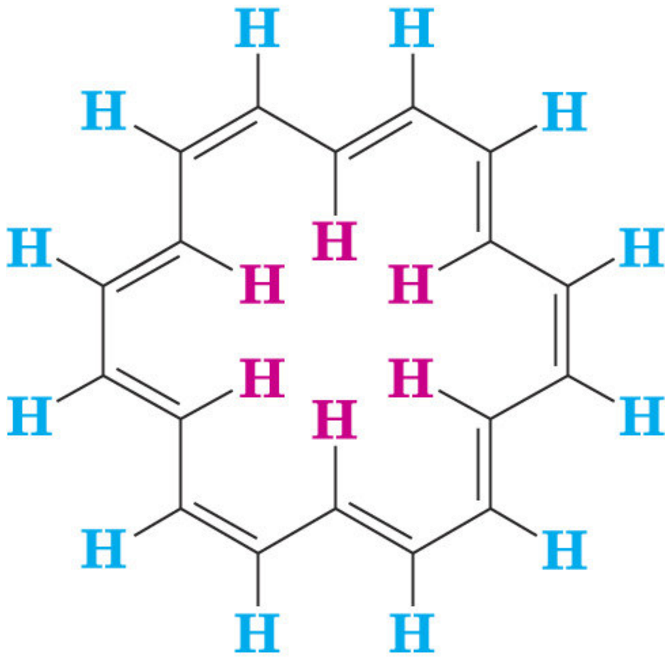
## NMR Spectroscopy: Evidence for Electron Delocalization in Aromatic Compounds

- When benzene is placed in a strong magnetic field a π-electron ring current is induced which reinforces the applied magnetic field at the location of the protons
  - The net effect is that the protons of benzene are highly deshielded (their signal is a singlet at δ 7.27)

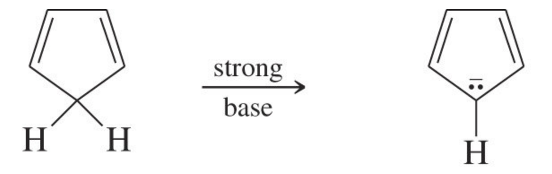


- Generally protons at the periphery of aromatic compounds are highly deshielded
  - Deshielding of these protons is physical evidence for aromaticity

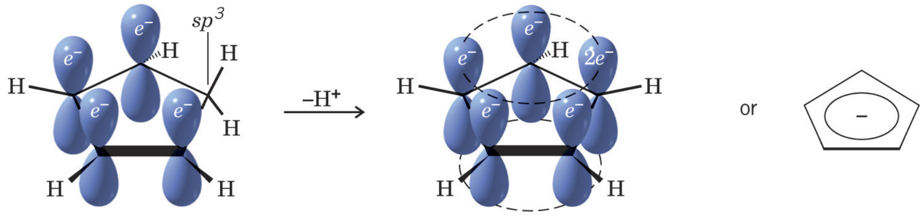
- The ring current of aromatic systems also provides regions of great sheilding
  - In large annulenes the internal protons tend to be highly sheilded
  - In [18]annulenes the protons along the outside of the ring (pink) appear at δ 9.3 whereas those on the inside of the ring (blue) appear at δ -3.0 (very highly shielded)



- **Aromatic Ions**
  - ➔ **Cyclopentadiene is unusually acidic ($pK_a$ = 16) because it becomes the aromatic cyclopentadienyl anion when a proton is removed**
    - **Cyclopentadienyl anion has 6 π electrons in a cyclic, continuous π-electron system, and hence follows the 4n + 2 rule for aromaticity**

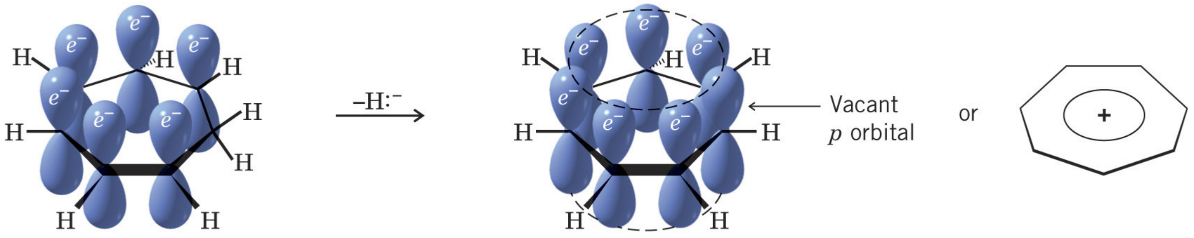


**Cyclopentadiene** **Cyclopentadienyl anion**



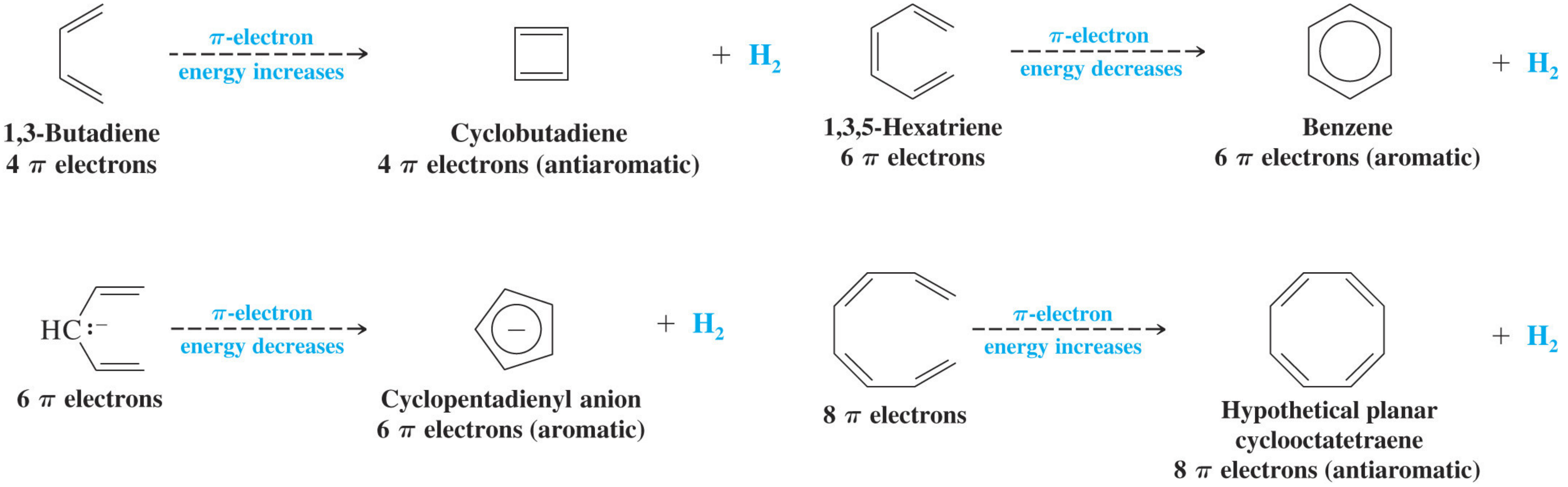
**Cyclopentadiene** **Cyclopentadienyl anion**

  - ➔ **Cycloheptatriene is not aromatic because its π electrons are not delocalized around the ring (the *sp*³-hybridized $CH_2$ group is an “insulator”)**
    - **Lose of hydride produces the aromatic cycloheptatrienyl cation (tropylium cation)**



**Cycloheptatriene** **Cycloheptatrienyl cation**

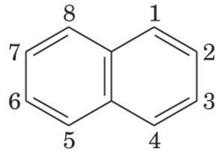
- **Aromatic, Antiaromatic, and Nonaromatic Compounds**
  - ➔ A comparison of cyclic annulenes with their acyclic counterparts provides a measures of the stability conferred by aromaticity
    - If the ring has lower π-electron energy than the open chain, then it is <u>aromatic</u>
    - If the ring has the same π-electron energy as the open chain, then it is <u>nonaromatic</u>
    - If the ring has higher π-electron energy than the open chain, then it is <u>antiaromatic</u>
  - ➔ Benzene and cylcopentadientl anion are aromatic
  - ➔ Cyclobutadiene is antiaromatic
    - Cyclooctatetraene, if it were planar, would be antiaromatic



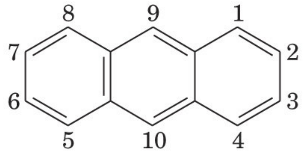
# ♦ Other Aromatic Compounds

## ● Benzenoid Aromatic Compounds

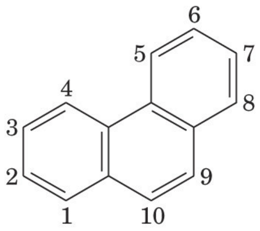
➔ **Polycyclic benzenoid aromatic compounds have two or more benzene rings fused together**



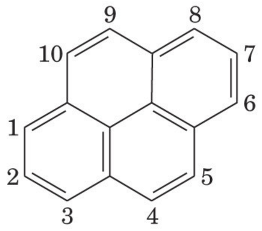
**Naphthalene**
$C_{10}H_8$



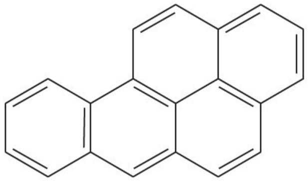
**Anthracene**
$C_{14}H_{10}$



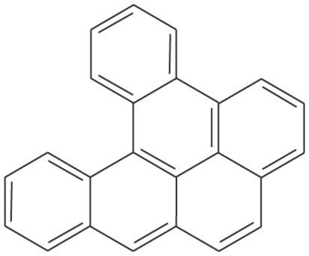
**Phenanthrene**
$C_{14}H_{10}$



**Pyrene**
$C_{16}H_{10}$

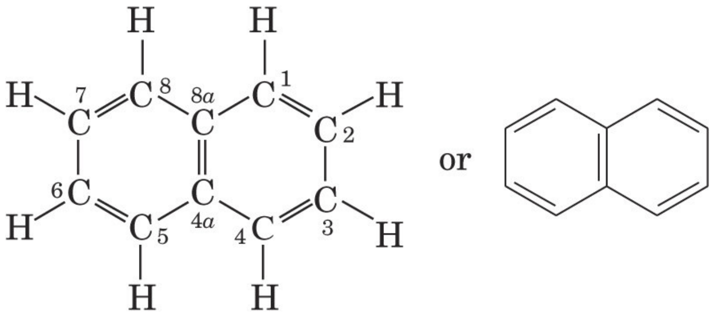


**Benzo[*a*]pyrene**
$C_{20}H_{12}$

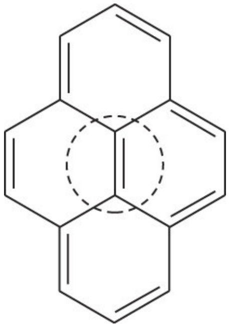


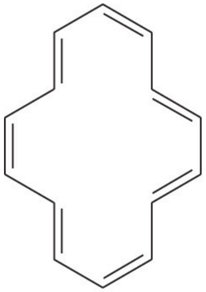
**Dibenzo[*a*,*l*]pyrene**
$C_{24}H_{14}$

- ➔ **Naphthalene can be represented by three resonance structures**
  - **The most important resonance structure is shown below**
  - **Calculations show that the 10 π electrons of napthalene are delocalized and that it has substantial resonance energy**

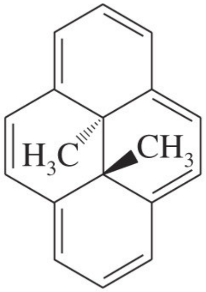


- ➔ **Pyrene has 16 π electrons, a non-Huckel number, yet is known to be aromatic**
  - **Ignoring the central double bond, the periphery of pyrene has 14 π electrons, a Huckel number, and on this basis it resembles the aromatic [14]annulene**



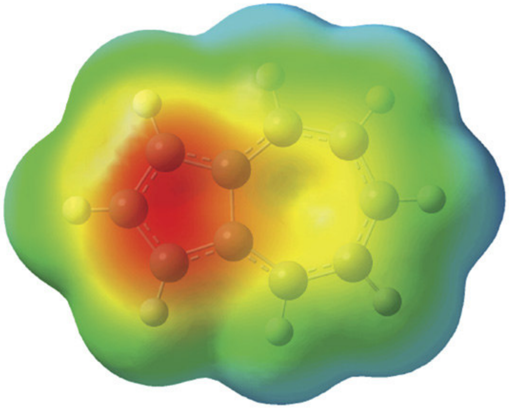


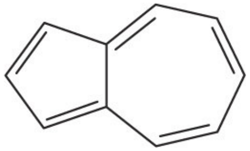
**[14]Annulene**



***trans*-15,16-Dimethyldihydropyrene**

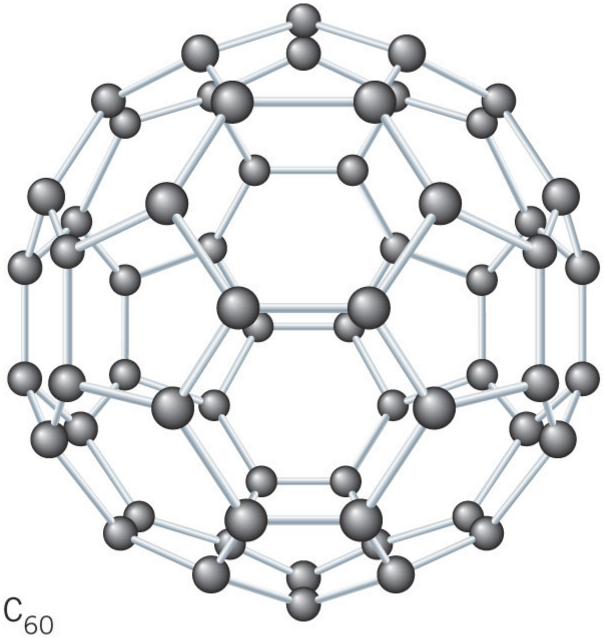
- **Nonbenzenoid Aromatic Compounds**
  - ➔ **Nonbenzenoid aromatic compounds do not contain benzene rings**
    - **Examples are cyclopentadienyl anion and the aromatic annulenes (except [6] annulene)**
  - ➔ **Azulene has substantial resonance energy and also substantial separation of charge, as shown in the electrostatic potential map**



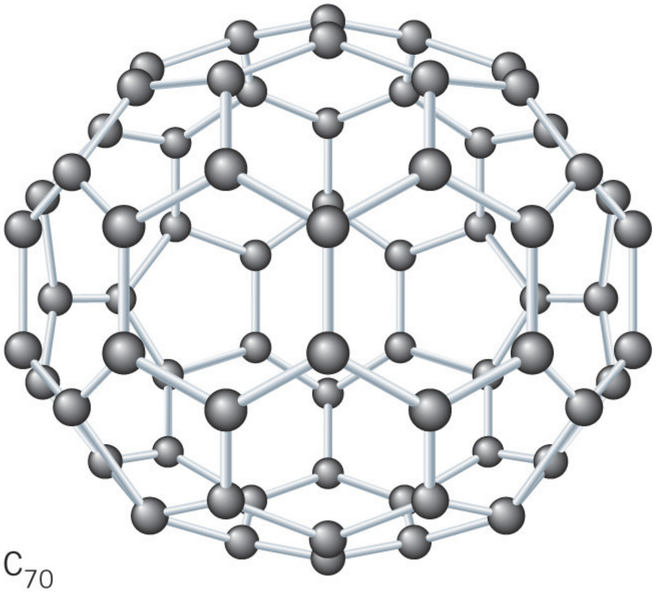


**Azulene**

- **Fullerenes**
  - ➔ **Buckminsterfullerene is a $C_{60}$ compound shaped like a soccer ball with interconnecting pentagons and hexagons**
    - **Each carbon is *sp*$^2$ hybridized and has bonds to 3 other carbons**
    - **Buckminsterfullerene is aromatic**
  - ➔ **Analogs of "Buckyballs" have been synthesized (*e.g.* $C_{70}$)**



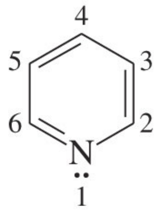
$C_{60}$



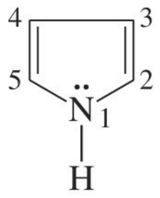
$C_{70}$

# ♦ Heterocyclic Aromatic Compounds

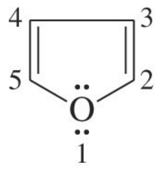
- **Heterocyclic compounds have an element other than carbon as a member of the ring**
- **Example of aromatic heterocyclic compounds are shown below**
  - **Numbering always starts at the heteroatom**



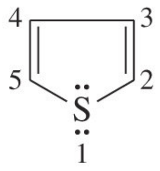
**Pyridine**



**Pyrrole**

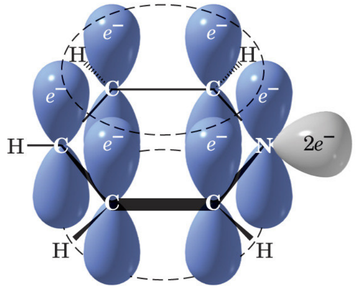


**Furan**

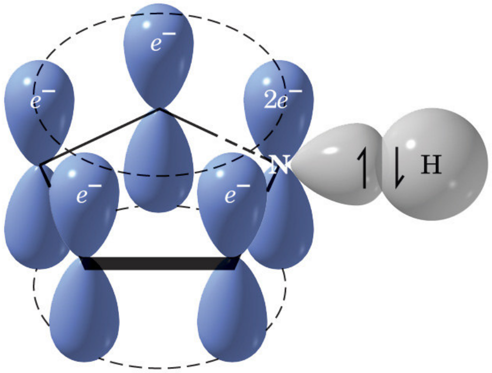


**Thiophene**

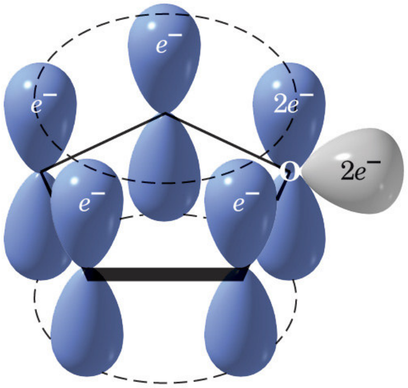
- **Pyridine has an *sp*$^2$ hybridized nitrogen**
  - **The *p* orbital on nitrogen is part of the aromatic π system of the ring**
  - **The nitrogen lone pair is in an *sp*$^2$ orbital orthogonal to the *p* orbitals of the ring; these electrons are not part of the aromatic system**
  - **The lone pair on nitrogen is available to react with protons and so pyridine is basic**

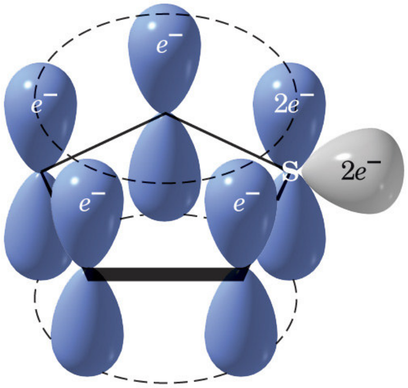


- **The nitrogen in pyrrole is *sp*$^2$ hybridized and the lone pair resides in the p orbital**
  - **This p orbital contains two electrons and participates in the aromatic system**
  - **The lone pair of pyrrole is part of the aromatic system and not available for protonation; pyrrole is therefore not basic**



- **In furan and thiophene an electron pair on the heteroatom is also in a *p* orbital which is part of the aromatic system**



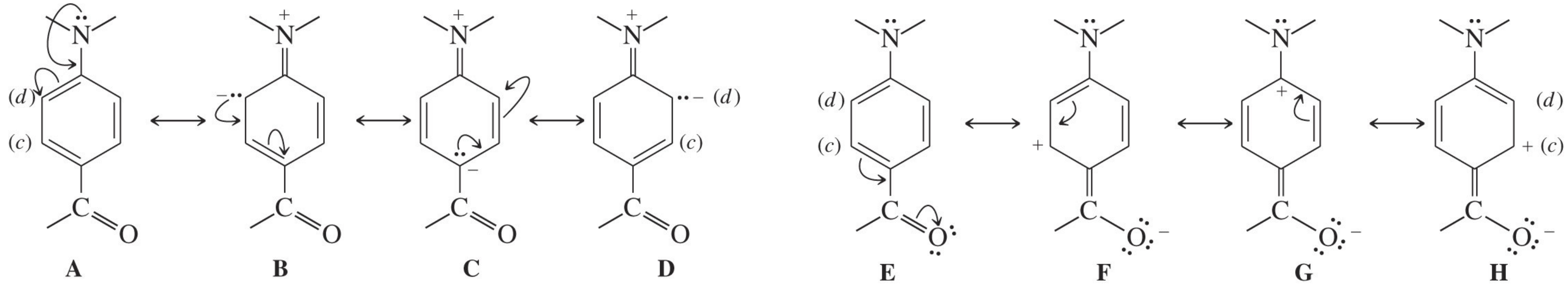


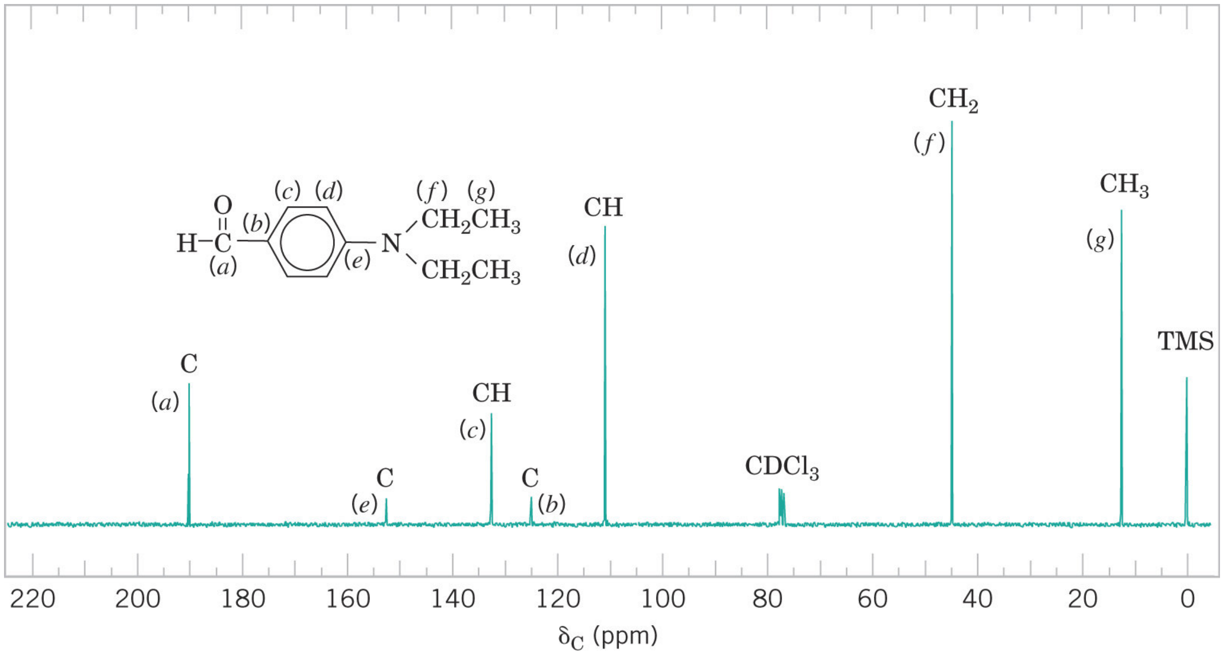
# ♦ Spectroscopy of Aromatic Compounds

- $^1$H NMR Spectra
  - ➔ Protons of benzene derivatives are highly deshielded and appear in the region $\delta$ 6.0 to $\delta$ 9.5
    - A ring current is induced in the benzene ring that reinforces the applied magnetic field in the region of the protons in benzene
    - In large annulenes protons pointing into the ring are highly sheilded
- $^{13}$C NMR Spectra
  - ➔ Aromatic carbons generally appear in the $\delta$ 100-170 region
    - DEPT spectra will show these carbons to have one or no protons attached

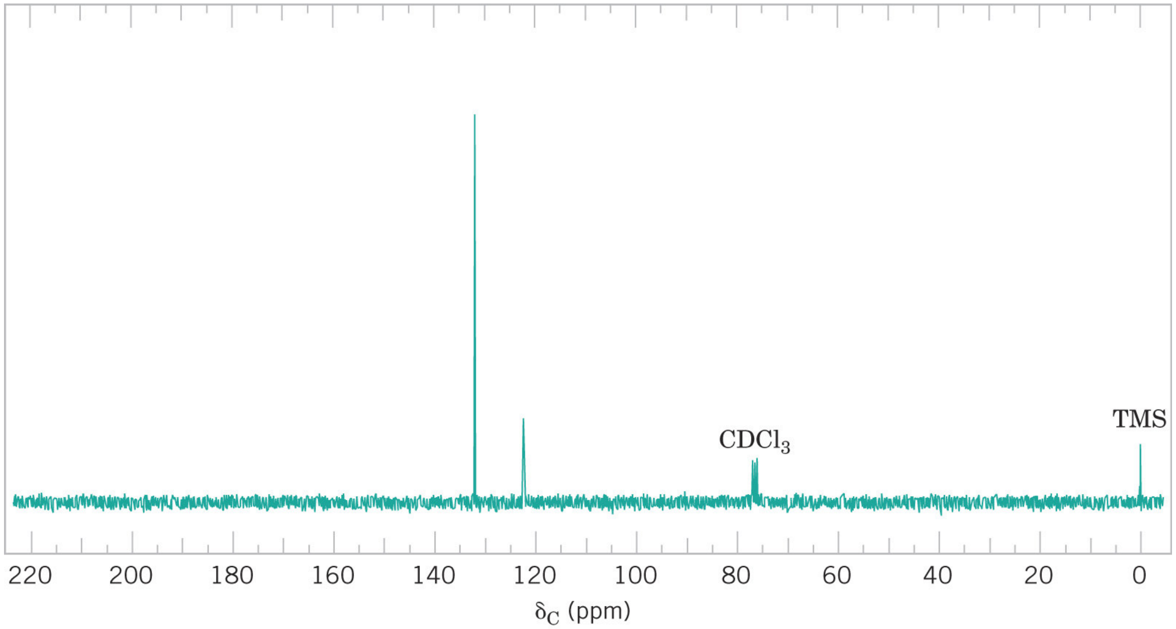
## ➔Example : the spectrum of 4-*N,N*-diethylaminobenzaldehyde

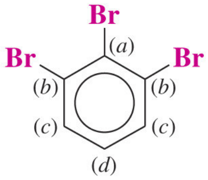
- **The assignment of carbons (d) and (c) is possible because carbons (d) should have higher electron density than carbons (c), based on resonance structures**



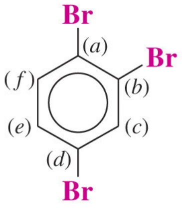


- **Given a molecular formula or mass spectrometric data, $^{13}$C NMR can be used to recognize compounds with high symmetry**
  - **The spectrum below corresponds to the last isomer which can have only two peaks**

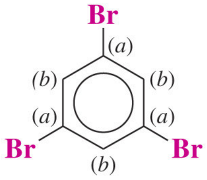




**1,2,3-Tribromobenzene**

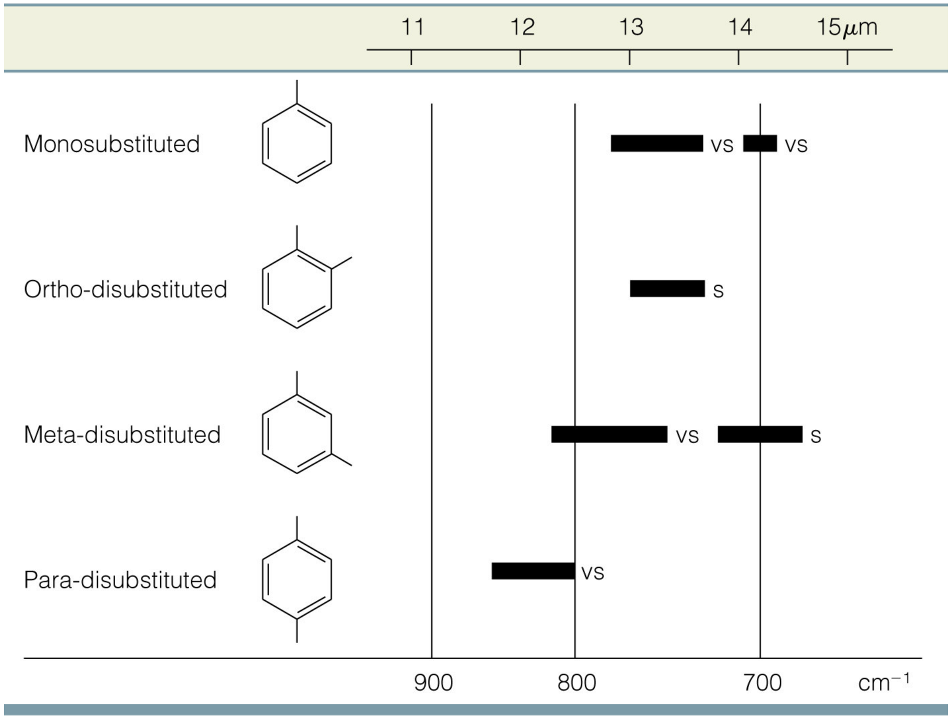


**1,2,4-Tribromobenzene**



**1,3,5-Tribromobenzene**

- **Infrared Spectra of Substituted Benzenes**
  - ➔ **Benzene derivatives show several characteristic frequencies**
    - **C-H Stretching occurs near 3030 cm$^{-1}$**
    - **Stretching motions of the ring give bands at 1450-1600 cm$^{-1}$ and two bands near 1500 and 1600 cm$^{-1}$**
  - ➔ **Monosubstituted benzenes show two strong absorptions at 690-710 cm$^{-1}$ and 730-770 cm$^{-1}$**
  - ➔ **Disubstituted benzenes show the following absorptions**



- **Ultraviolet-Visible Spectra of Aromatic Compounds**
  - ➔ **Benzene derivatives give an absorption band of moderate intensity near 205 nm and a less intense band at 250-275 nm**

- **Mass Spectra of Aromatic Compounds**
  - ➔ **The major ion in the mass spectrum of alkyl benzenes is *m/z* 91, which corresponds to a benzyl cation ($C_6H_5CH_2^+$), which rearranges to a tropylium ion ($C_7H_7^+$)**
  - ➔ **Another common ion is the phenyl cation ($C_6H_5^+$)**