Benzene and Aromaticity

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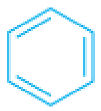
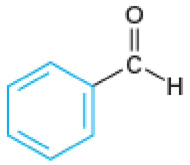
Reference Text Book:

- John McMurry "Organic Chemistry" 9th Edition, Cengage Learning, USA **(2016).**

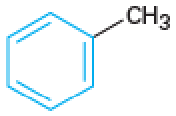
In the early days of organic chemistry, the word *aromatic* was used to describe such fragrant substances as benzaldehyde (from cherries, peaches, and almonds), toluene (from Tolu balsam), and benzene (from coal distillate). It was soon realized, however, that substances grouped as aromatic differed from most other organic compounds in their chemical behavior.



Benzene

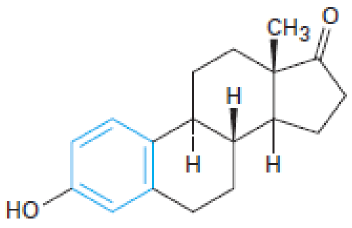


Benzaldehyde

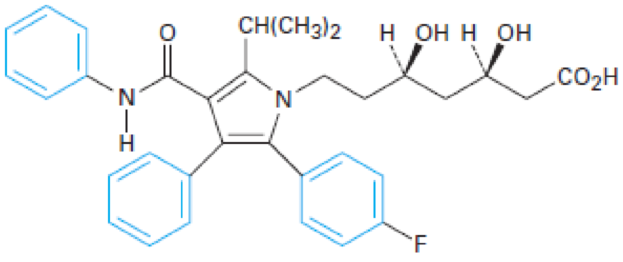


Toluene

Today, the association of aromaticity with fragrance has long been lost, and we now use the word **aromatic** to refer to the class of compounds that contain six-membered benzene-like rings with three double bonds. Many naturally occurring compounds are aromatic in part, including steroids such as estrone and well-known pharmaceuticals such as the cholesterol-lowering drug atorvastatin, marketed as Lipitor. Benzene itself causes a depressed white blood cell count (leukopenia) on prolonged exposure and should not be used as a laboratory solvent.



Estrone



Atorvastatin
(Lipitor)

Naming Aromatic Compounds

Simple aromatic hydrocarbons come from two main sources: coal and petroleum.

Coal is an enormously complex mixture consisting primarily of large arrays of conjoined benzene-like rings. Thermal breakdown of coal occurs when it is heated to 1000 °C in the absence of air, and a mixture of volatile products called *coal tar* boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and a host of other aromatic compounds **(Figure-1)**.

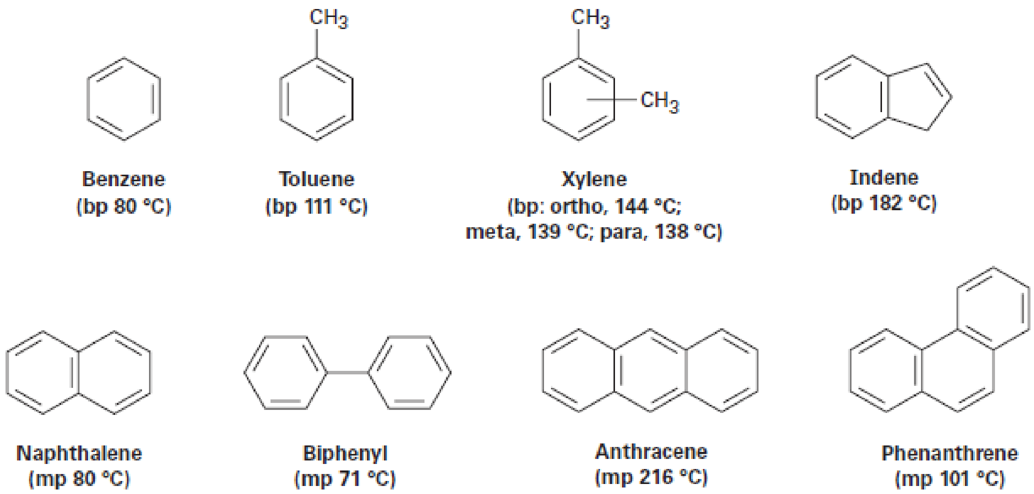
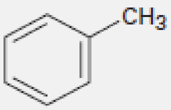
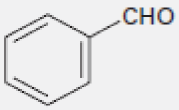
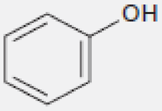
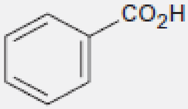
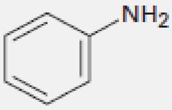
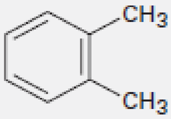
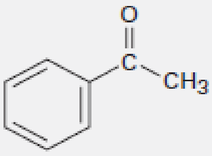
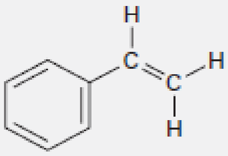


Figure-1 Some aromatic hydrocarbons found in coal tar.

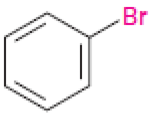
Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes. During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure.

Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. IUPAC rules discourage the use of most such names but do allow some of the more widely used ones to be retained **(Table-1)**. Thus, methylbenzene is known commonly as *toluene;* hydroxybenzene as *phenol;* aminobenzene as *aniline;* and so on.

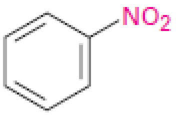
Table-1 Common Names of Some Aromatic Compounds

Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		*ortho*-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

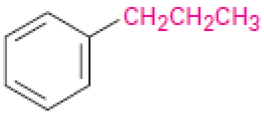
Monosubstituted benzenes are named systematically in the same manner as other hydrocarbons, with -*benzene* as the parent name. Thus, C_6H_5Br is bromobenzene, $C_6H_5NO_2$ is nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene.



Bromobenzene

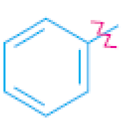


Nitrobenzene

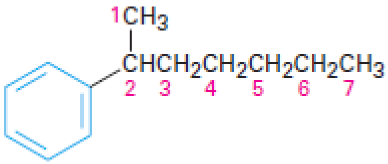


Propylbenzene

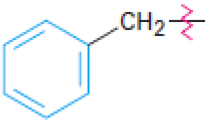
Alkyl-substituted benzenes are sometimes referred to as **arenes** and are named in different ways depending on the size of the alkyl group. If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is referred to as an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is referred to as a phenyl-substituted alkane. The name **phenyl**, pronounced **fen**-nil and sometimes abbreviated as Ph or ϕ (Greek *phi*), is used for the $-C_6H_5$ unit when the benzene ring is considered a substituent. In addition, the name **benzyl** is used for the $C_6H_5CH_2-$ group.



A phenyl group

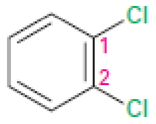


2-Phenylheptane

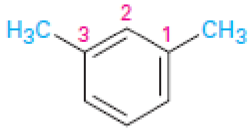


A benzyl group

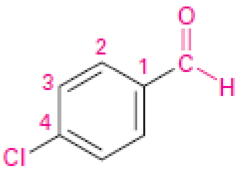
Disubstituted benzenes are named using the prefixes **ortho (*o*)**, **meta (*m*)**, or **para (*p*)**. An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its substituents in a 1,4 relationship.



ortho-Dichlorobenzene
1,2 disubstituted

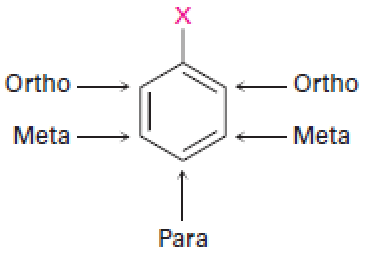


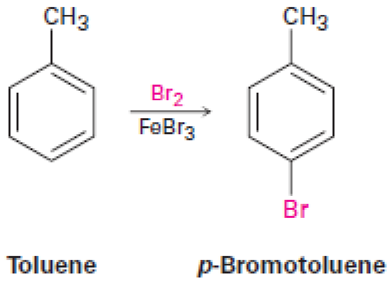
meta-Dimethylbenzene
(meta-xylene)
1,3 disubstituted



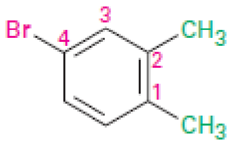
para-Chlorobenzaldehyde
1,4 disubstituted

The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, “Reaction occurs at the para position”—in other words, at the position para to the methyl group already present on the ring.

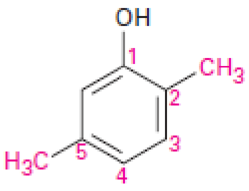




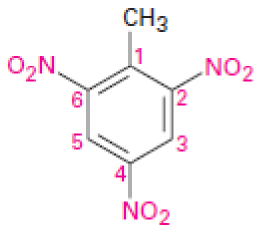
As with cycloalkanes, benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the second substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name.



4-Bromo-1,2-dimethylbenzene



2,5-Dimethylphenol

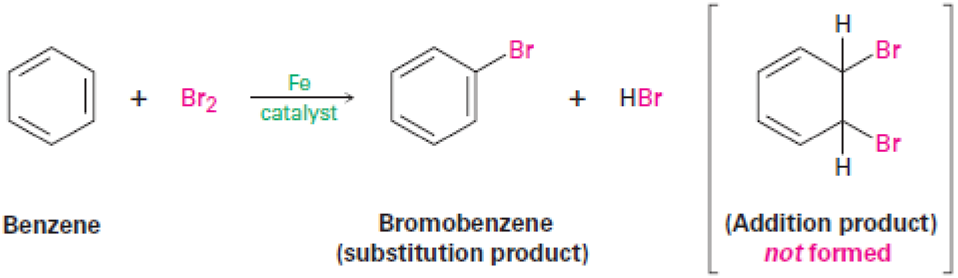


2,4,6-Trinitrotoluene (TNT)

Note in the second and third examples shown that *-phenol* and *–toluene* are used as the parent names rather than *-benzene.* Any of the monosubstituted aromatic compounds shown in Table-1 can serve as a parent name, with the principal substituent (-OH in phenol or -CH_3 in toluene) attached to C1 on the ring.

Structure and Stability of Benzene

Benzene (C_6H_6) has six fewer hydrogens than the corresponding six-carbon cycloalkane (C_6H_{12}) and is clearly unsaturated, usually being represented as a six-membered ring with alternating double and single bonds. Benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions. Cyclohexene, for instance, reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene only reacts slowly with Br_2 and gives the *substitution* product C_6H_5Br.



We can get a quantitative idea of benzene's stability by measuring heats of hydrogenation. Cyclohexene, an isolated alkene, has Δ*H*°hydrog =-118 kJ/mol (-28.2 kcal/mol), and 1,3-cyclohexadiene, a conjugated diene, has Δ*H*°hydrog = -230 kJ/mol (-55.0 kcal/mol). As noted, this value for 1,3-cyclohexadiene is a bit less than twice that for cyclohexene because conjugated dienes are more stable than isolated dienes. Carrying the process one step further, we might expect Δ*H*°hydrog for "cyclohexatriene" (benzene) to be a bit less than -356 kJ/mol, or three times the cyclohexene value. The actual value, however, is -206 kJ/mol, some 150 kJ/mol (36 kcal/mol) less than expected. Because of this difference in actual and expected energy released during hydrogenation, benzene must have 150 kJ/mol less energy to begin with. In other words, benzene is more stable than expected by 150 kJ/mol **(Figure-2)**.

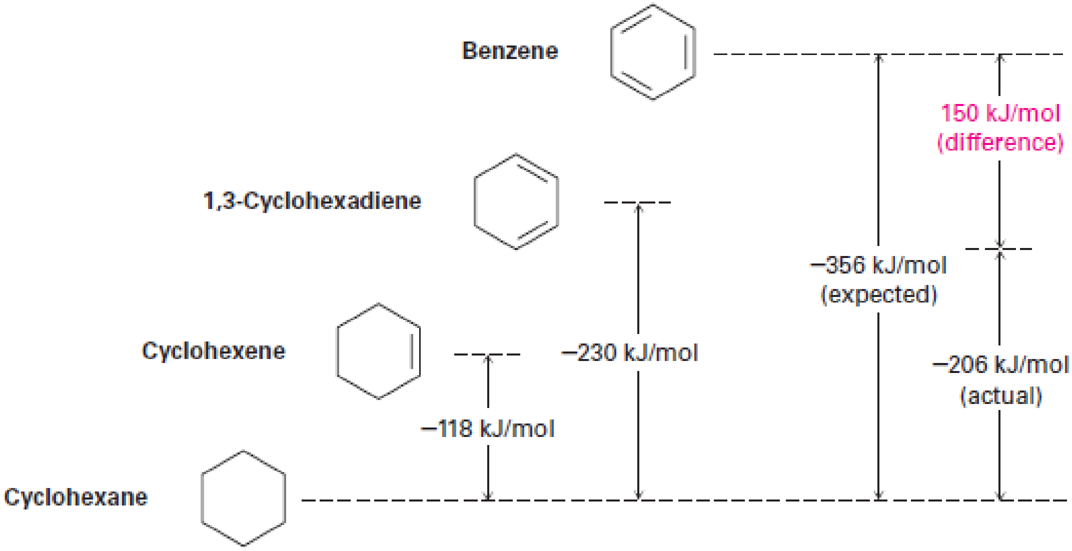
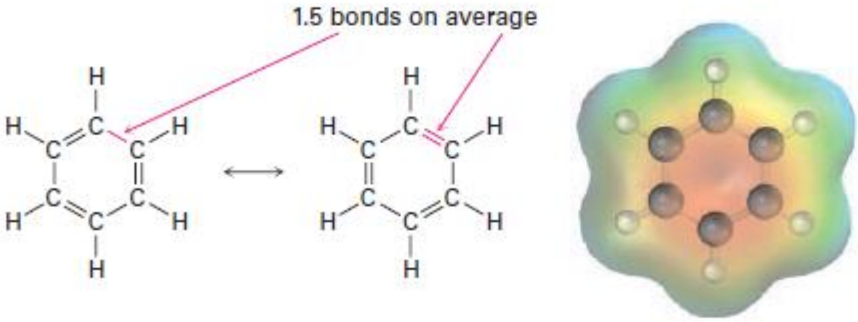


Figure-2 A comparison of the heats of hydrogenation for cyclohexene, 1,3 cyclohexadiene, and benzene. Benzene is 150 kJ/mol (36 kcal/mol) more stable than might be expected for "cyclohexatriene."

Further evidence for the unusual nature of benzene is that all its carbon–carbon bonds have the same length (139 pm) intermediate between typical single (154 pm) and double (134 pm) bonds. In addition, an electrostatic potential map shows that the electron density in all six C-C bonds is identical.

Thus, benzene is a planar molecule with the shape of a regular hexagon. All C-C-C bond angles are 120°, all six carbon atoms are *sp*2-hybridized, and each carbon has a *p* orbital perpendicular to the plane of the six-membered ring.



Because all six carbon atoms and all six *p* orbitals in benzene are equivalent, it's impossible to define three localized *Π* bonds in which a given *p* orbital overlaps only one neighboring *p* orbital. Rather, each *p* orbital overlaps equally well with both neighboring *p* orbitals, leading to a picture of benzene in which all six *Π* electrons are free to move about the entire ring **(Figure-3b)**.

In resonance terms, benzene is a hybrid of two equivalent forms. Neither form is correct by itself; the true structure of benzene is somewhere in between the two resonance forms but is impossible to draw with our usual conventions. Because of this resonance, benzene is more stable and less reactive than a typical alkene.

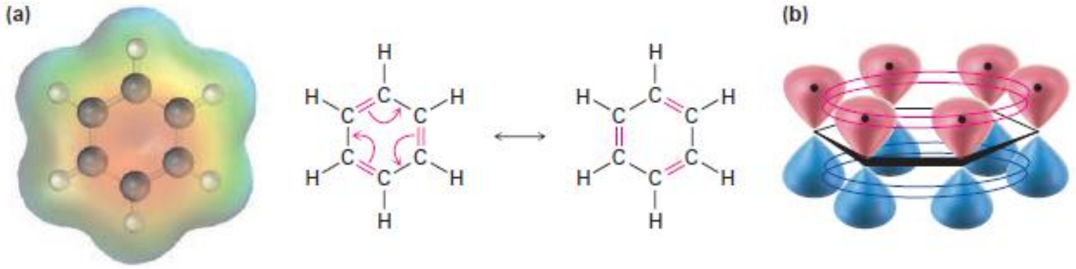
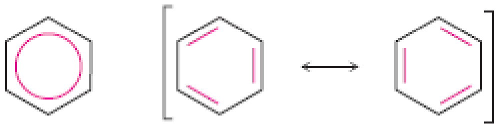


Figure-3 **(a)** An electrostatic potential map of benzene and **(b)** an orbital picture. Each of the six carbon atoms has a *p* orbital that can overlap equally well with neighboring *p* orbitals on both sides. As a result, all C-C bonds are equivalent and benzene must be represented as a hybrid of two resonance forms.

Chemists sometimes represent the two benzene resonance forms by using a circle to indicate the equivalence of the carbon–carbon bonds. This representation has to be used carefully, however, because it doesn't indicate the number of *Π* electrons in the ring. Benzene and other aromatic compounds will be represented by a single line-bond structure. We'll be able to keep count of *Π* electrons this way but must be aware of the limitations of the drawings.



Alternative representations of benzene. The "circle" representation must be used carefully since it doesn't indicate the number of π electrons in the ring.

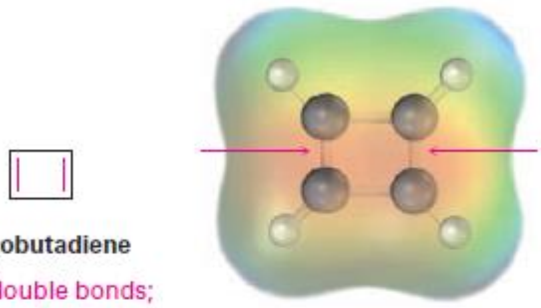
Aromaticity and the Hückel (4*n* + 2) Rule

Let's list what we've said thus far about benzene and, by extension, about other benzene-like aromatic molecules.

- Benzene is cyclic and conjugated.
- Benzene is unusually stable, having a heat of hydrogenation 150 kJ/mol less negative than we might expect for a conjugated cyclic triene.
- Benzene is planar and has the shape of a regular hexagon. All bond anglesare 120°, all carbon atoms are *sp*2-hybridized, and all carbon–carbon bond lengths are 139 pm.
- Benzene undergoes substitution reactions that retain the cyclic conjugation rather than electrophilic addition reactions that would destroy it.
- Benzene can be described as a resonance hybrid whose structure is intermediate between two line-bond structures.

This list would seem to be a good description of benzene and otheraromatic molecules, but it isn't enough. Something else, called the **Hückel (4*n* + 2) rule**, is needed to complete a description of aromaticity. According to a theory devised in 1931 by the German physicist Erich Hückel, a molecule is aromatic only if it has a planar, monocyclic system of conjugation and contains a total of 4*n* + 2 *Π electrons*, where *n* is an integer (*n* = 0, 1, 2, 3, . . .). In other words, only molecules with 2, 6, 10, 14, 18, . . . *Π* electrons can be aromatic. Molecules with 4*n* *Π* electrons (4, 8, 12, 16, . . .) can't be aromatic, even though they may be cyclic, planar, and apparently conjugated. In fact, planar, conjugated molecules with 4*n* *Π* electrons are said to be **antiaromatic** because delocalization of their *Π* electrons would lead to their destabilization. Let's look at several examples to see how the Hückel 4*n* + 2 rule works.

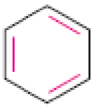
- **Cyclobutadiene** has four *Π* electrons and is antiaromatic. The *Π* electrons are localized in two double bonds rather than delocalized around the ring, as indicated by the electrostatic potential map.



Cyclobutadiene

Two double bonds; four π electrons

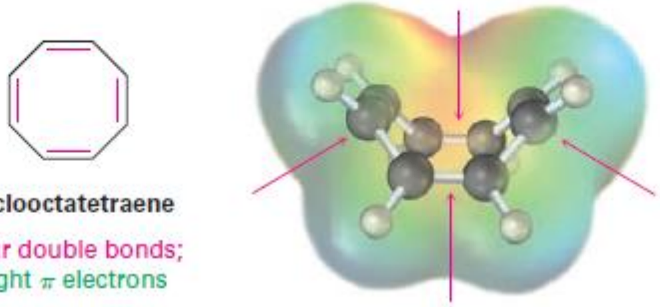
- **Benzene** has six Π electrons ($4n + 2 = 6$ when $n = 1$) and is aromatic.



Benzene

Three double bonds; six π electrons

- **Cyclooctatetraene** has eight Π electrons and is not aromatic. The Π electrons are localized into four double bonds rather than delocalized around the ring, and the molecule is tub-shaped rather than planar. It has no cyclic conjugation because neighboring *p* orbitals don't have the necessary parallel alignment for overlap, and it resembles an open-chain polyene in its reactivity.

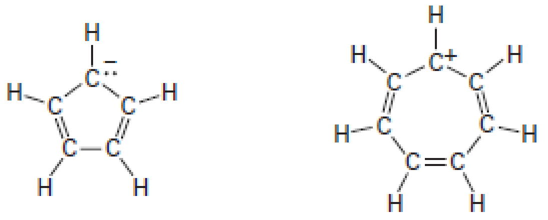


Cyclooctatetraene

Four double bonds; eight π electrons

Aromatic Ions

According to the Hückel criteria for aromaticity, a molecule must be cyclic, conjugated (nearly planar with a *p* orbital on each atom), and have $4n + 2$ Π electrons. Nothing in this definition says that the number of Π electrons must be the same as the number of atoms in the ring or that the substance must be neutral. In fact, the numbers can differ and the substance can be an ion. Thus, both the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic even though both are ions and neither contains a six-membered ring.



Cyclopentadienyl anion Cycloheptatrienyl cation

Six π electrons; aromatic ions

To see why the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic, imagine starting from the related neutral hydrocarbons, 1,3-cyclopentadiene and 1,3,5-cycloheptatriene, and removing one hydrogen from the saturated CH_2 carbon in each. If that carbon then rehybridizes from *sp*3 to *sp*2, the resultant products would be fully conjugated, with a *p* orbital on every carbon. There are three ways in which the hydrogen might be removed.

- The hydrogen can be removed with *both* electrons (H**:** $^-$) from the C-H bond, leaving a carbocation as product.
- The hydrogen can be removed with *one* electron (H•) from the C-H bond, leaving a carbon radical as product.
- The hydrogen can be removed with *no* electrons (H^+) from the C-H bond, leaving a carbanion as product.

All the potential products formed by removing a hydrogen from 1,3-cyclopentadiene and from 1,3,5-cycloheptatriene can be drawn with numerous resonance structures, but Hückel's rule predicts that only the six-*Π*-electron cyclopentadienyl anion and cycloheptatrienyl cation should be aromatic. The other products are predicted by the $4n + 2$ rule to be unstable and antiaromatic **(Figure-4)**.

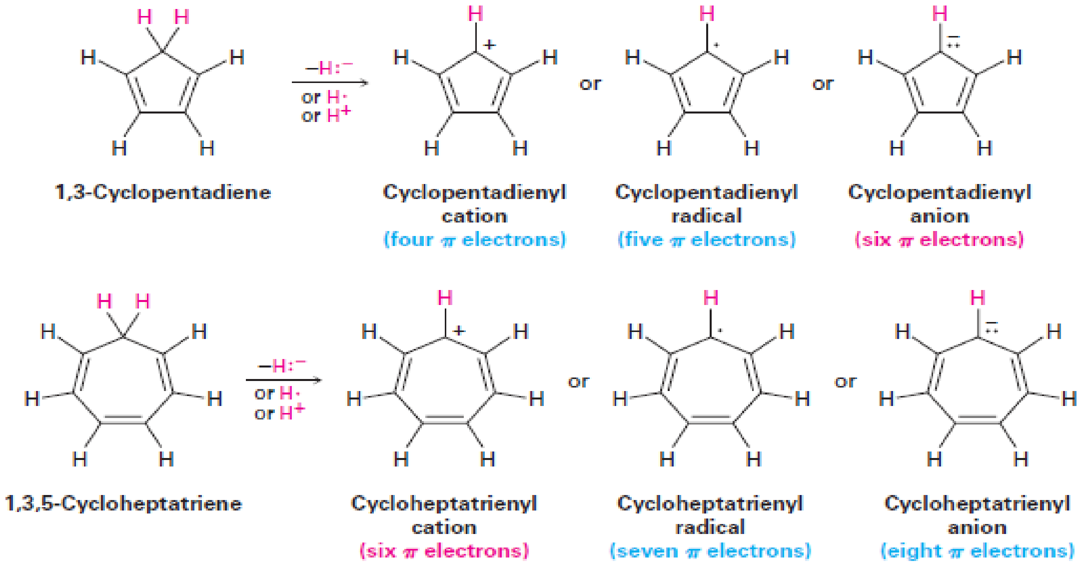


Figure-4 The aromatic six-*Π*-electron cyclopentadienyl anion and the six-*Π*-electron cycloheptatrienyl cation. The anion can be formed by removing a hydrogen ion (H^+) from the CH_2 group of 1,3-cyclopentadiene. The cation can be generated by removing a hydride ion (H**:**-) from the CH_2 group of 1,3,5-cycloheptatriene.

In practice, both the four-*p*-electron cyclopentadienyl cation and the five *Π*-electron cyclopentadienyl radical are highly reactive and difficult to prepare. Neither shows any sign of the stability expected for an aromatic system. The six-*Π*-electron cyclopentadienyl anion, by contrast, is easily prepared and remarkably stable **(Figure-5a)**. In fact, the anion is so stable and easily formed that 1,3-cyclopentadiene is one of the most acidic hydrocarbons known, with p*K*a = 16, a value comparable to that of water.

In the same way, the seven-*Π*-electron cycloheptatrienyl radical and eight *Π*- electron anion are reactive and difficult to prepare, while the six-*Π*-electron cycloheptatrienyl cation is extraordinarily stable (Figure-7b). In fact, the cycloheptatrienyl cation was first prepared more than a century ago by reaction of 1,3,5-cycloheptatriene with Br_2, although its structure was not recognized at the time.

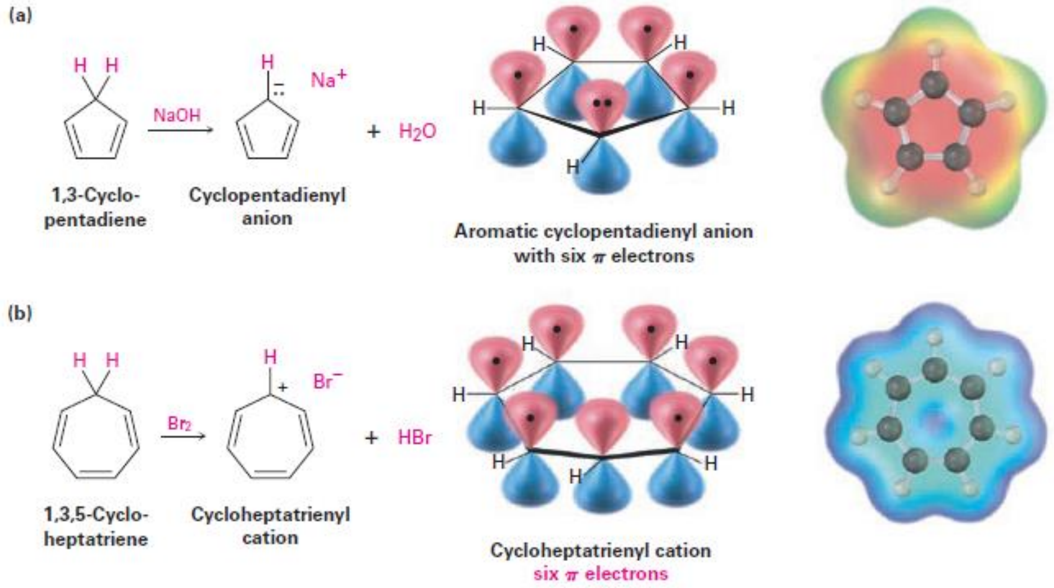
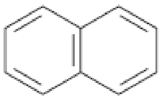


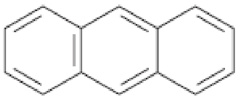
Figure-5 **(a)** The aromatic cyclopentadienyl anion, showing cyclic conjugation and six *Π* electrons in five *p* orbitals, and **(b)** the aromatic cycloheptatrienyl cation, showing cyclic conjugation and six *Π* electrons in seven *p* orbitals. Electrostatic potential maps indicate that both ions are symmetrical, with the charge equally shared among all atoms in each ring.

Polycyclic Aromatic Compounds

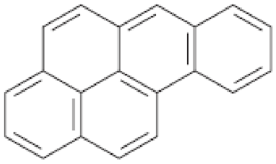
The Hückel rule is only strictly applicable to monocyclic compounds, but the general concept of aromaticity can be extended to include *polycyclic* aromatic compounds. Naphthalene, with two benzene-like rings fused together; anthracene, with three rings; benzo[a]pyrene, with five rings; and coronene, with six rings, are all well-known aromatic hydrocarbons. Benzo[a]pyrene is particularly interesting because it is one of the cancer-causing substances found in tobacco smoke.



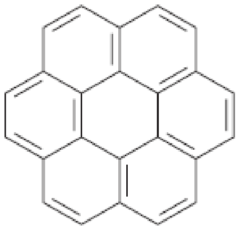
Naphthalene



Anthracene

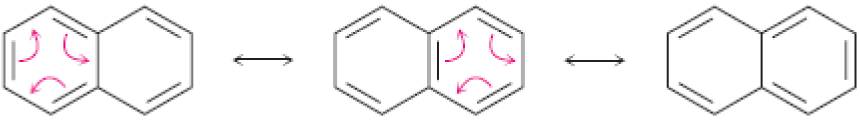


Benzo[a]pyrene



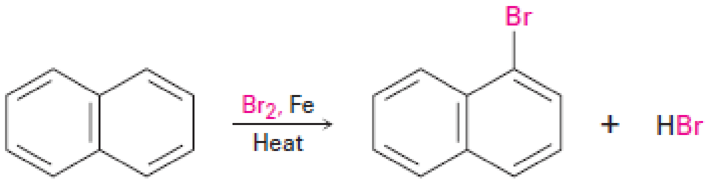
Coronene

All polycyclic aromatic hydrocarbons can be represented by a number of different resonance forms. Naphthalene, for instance, has three.



Naphthalene

Naphthalene and other polycyclic aromatic hydrocarbons show many of the chemical properties associated with aromaticity. Thus, measurement of its heat of hydrogenation shows an aromatic stabilization energy of approximately 250 kJ/mol (60 kcal/mol). Furthermore, naphthalene reacts slowly with electrophiles such as Br_2 to give substitution products rather than double-bond addition products.



Naphthalene **1-Bromonaphthalene (75%)**

The aromaticity of naphthalene is explained by the orbital picture in **Figure-6**. Naphthalene has a cyclic, conjugated Π electron system, with *p* orbital overlap both along the ten-carbon periphery of the molecule and across the central bond. Since ten Π electrons is a Hückel number, there is Π electron delocalization and consequent aromaticity in naphthalene.

Naphthalene

Figure-6 An orbital picture and electrostatic potential map of naphthalene, showing that the ten Π electrons are fully delocalized throughout both rings.