1 Aromaticity

Aims

By the end of this chapter, you should understand:

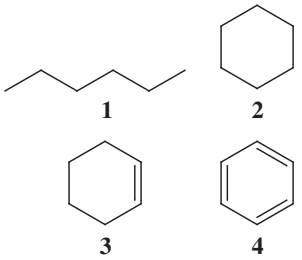
- The structure of benzene
- The concept of aromaticity and its application to various organic systems
- The fundamentals of naming derivatives of benzene

1.1 Introduction

The classification of organic compounds is based on the structure of the molecules. **Aliphatic** compounds have open-chain structures such as hexane (**1**) and can contain single (C–C), double (C=C) and triple (C≡C) bonds. In **alicyclic** molecules, the carbon atoms form a cyclic structure, as in cyclohexane (**2**) and cyclohexene (**3**).

Aromatic compounds are unsaturated cyclic molecules that possess additional stability as a result of the arrangement of π-electrons associated with the unsaturation of the ring system. This book will concentrate on the chemistry of benzene (**4**) and its derivatives and related polynuclear hydrocarbons. Aromatic compounds are also known as **arenes**; they can be **carbocyclic**, indicating that the ring skeleton contains only carbon atoms, or **heterocyclic**, with at least one atom other than carbon in the ring. These heteroatoms are typically N, O or S. Heterocyclic compounds, which can be aromatic or alicyclic, are covered in another book in this series.

Initially, we will look at what distinguishes aromatic compounds from other cyclic molecules and how chemists' understanding of aromaticity has developed up to the present day.



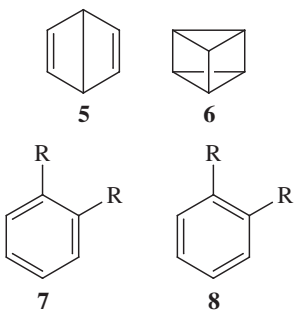
The term "aromatic" acknowledges the fact that many fragrant compounds contain benzene rings, whilst the term "aliphatic" is derived from the Greek word for fat or oil. Benzene was isolated in 1825 by Faraday from whale oil and in 1845 by Hofmann from coal tar. Benzene is a colourless, flammable liquid, with a boiling point of 80 °C. It is carcinogenic.

1.2 Structure of Benzene

Based on elemental composition and relative molecular mass determinations, the formula of benzene was found to be C_6H_6. The saturated hydrocarbon hexane has the molecular formula C_6H_{14} and therefore it was concluded that benzene was unsaturated. Kekulé in 1865 proposed the cyclic structure **4** for benzene in which the carbon atoms were joined by alternate single and double bonds. Certain reactions of benzene, such as the catalytic hydrogenation to cyclohexane, which involves the addition of six hydrogen atoms, confirmed that benzene was a ring compound and that it contained three double bonds. However, since benzene did not undergo addition reactions with HCl and HBr, it was concluded that these double bonds were different from those in ethene and other unsaturated aliphatic compounds.

Note that these structures were proposed before the electron had been discovered and before the idea of the covalent bond had been developed.

In 1867, Dewar proposed several possible structures for benzene, one of which was **5**. However, in 1874, Ladenburg proved experimentally that all the hydrogen atoms of benzene were equivalent and suggested the prismatic structure **6**.



5 **6** **7** **8**

Kekulé's proposed structure **4** looks more in keeping with our current knowledge of benzene, although it does not explain how the double bonds differ from the aliphatic type. Furthermore, although the two structures **7** and **8** can be drawn for a 1,2-disubstituted benzene, only one such compound exists. Kekulé proposed that the equivalent structures **7** and **8** oscillated between each other, averaging out the single and double bonds so that the compounds were indistinguishable.

1.3 Stability of the Benzene Ring

Kekulé's proposals gained wide acceptance and were supported by the experimental work of Baeyer in the late 19th century, but these ideas did not explain the unusual stability of benzene. This is typified by its chemical reactions, which are almost exclusively substitution rather than the expected addition. Throughout this book there will be many examples of this property. In addition, physical properties such as enthalpies of hydrogenation and combustion are significantly lower than would be expected for the cyclohexatriene structure of Kekulé. The enthalpy of hydrogenation (ΔH) of the double bond in cyclohexene is –120 kJ mol^{-1} and that of cyclohexa-1,3-diene with two double bonds is almost twice that at –232 kJ mol^{-1}. Cyclohexatriene, if it existed, would be expected to have an enthalpy of hydrogenation of three times the value of cyclohexene, a ΔH of approximately –360 kJ mol^{-1}. However, the value for benzene is less exothermic than this comparison suggests, being only –209 kJ mol^{-1}. Thus benzene is 151 kJ mol^{-1} more stable than cyclohexatriene (Figure 1.1). This is known as the **resonance energy** of ben-

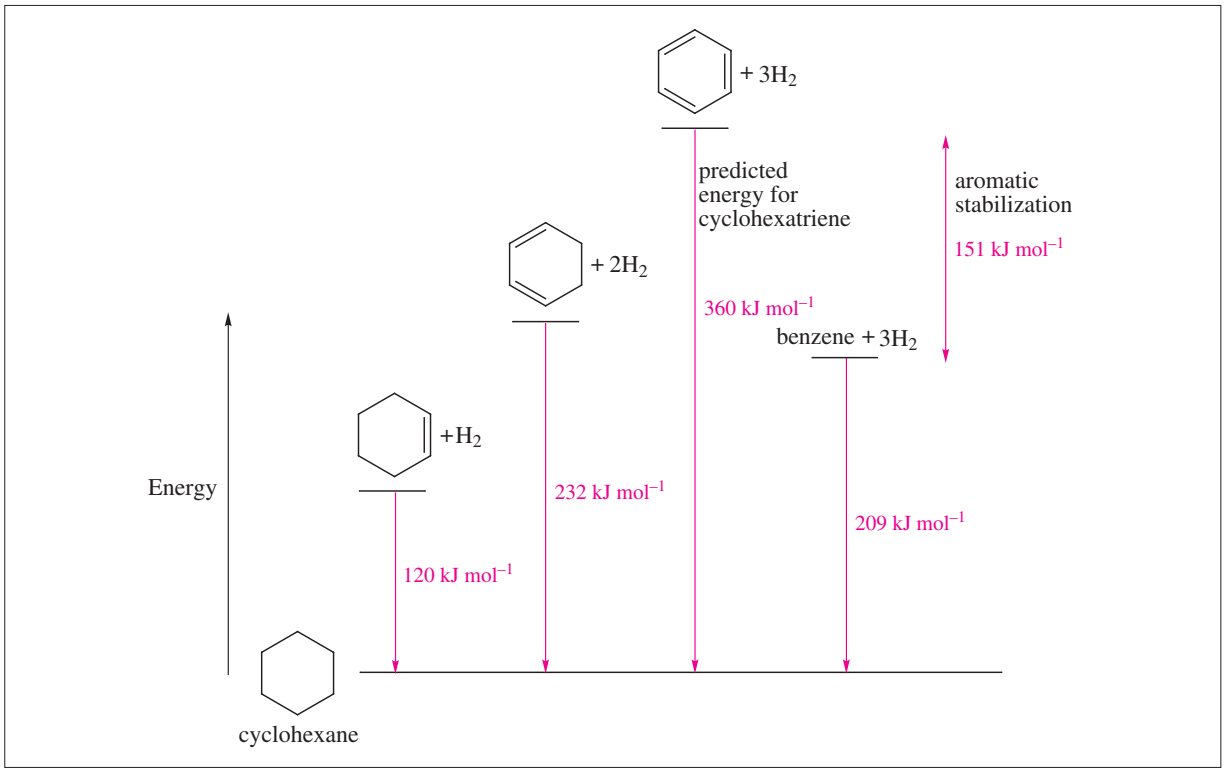


Figure 1.1 Hydrogenation of cyclohexene, cyclohexadiene and benzene

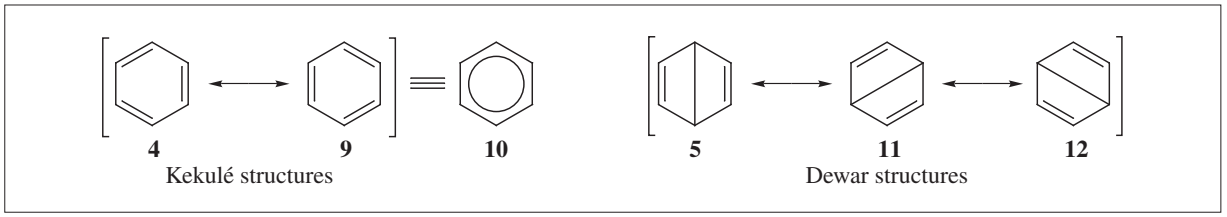
zene or its **aromatic stabilization**. This stabilizing feature dominates the chemistry of benzene and its derivatives.

1.3.1 Valence Bond Theory of Aromaticity

X-ray crystallographic analysis indicated that benzene is a planar, regular hexagon in which all the carbon–carbon bond lengths are 139 pm, intermediate between the single C–C bond in ethane (154 pm) and the C=C bond in ethene (134 pm), and therefore all have some double bond character. Thus the representation of benzene by one Kekulé structure is unsatisfactory. The picture of benzene according to valence bond theory is a resonance hybrid of the two Kekulé or canonical forms **4** and **9**, conventionally shown as in Figure 1.2, and so each carbon–carbon bond apparently has a bond order of 1.5.

A single bond has a bond order of 1 and a double bond a bond order of 2.

Figure 1.2



A double-headed arrow, ↔, is used to connect resonance structures.

It is emphasized that the circle inside a ring represents *exclusively* six π-electrons.

The three Dewar structures **5**, **11** and **12** (Dewar benzene) are also considered to contribute to the resonance hybrid (according to valence bond theory, approximately 20% in total) and to the extra stability. Dewar benzene has now been prepared. It is a bent, non-planar molecule and is not aromatic. It gradually reverts to benzene at room temperature. The Ladenburg structure, prismane (**6**), is an explosive liquid. Dewar benzene and prismane are valence isomers of benzene.

Although the canonical forms for benzene are imaginary and do not exist, the structure of benzene will be represented by one of the Kekulé structures throughout this book. This is common practice. A circle within a hexagon as in **10**, symbolic of the π-cloud, is sometimes used to represent benzene.

1.3.2 Molecular Orbital Theory of Benzene

The current understanding of the structure of benzene is based on molecular orbital (MO) theory. The six carbon atoms of benzene are sp^2 hybridized. The three sp^2 hybrid orbitals of each carbon atom, which are arranged at angles of 120°, overlap with those of two other carbon atoms and with the s orbital of a hydrogen atom to form the planar σ-bonded skeleton of the benzene ring. The p orbital associated with each carbon contains one electron and is perpendicular to the plane of the ring.

MO theory tells us that the six parallel p atomic orbitals are combined together to form six MOs, three of which are bonding orbitals and three anti-bonding. Figure 1.3 shows the relative energy levels of these MOs. The six π-electrons occupy the three bonding orbitals, all of lower energy than the uncombined p orbitals; the higher energy anti-bonding MOs are empty.

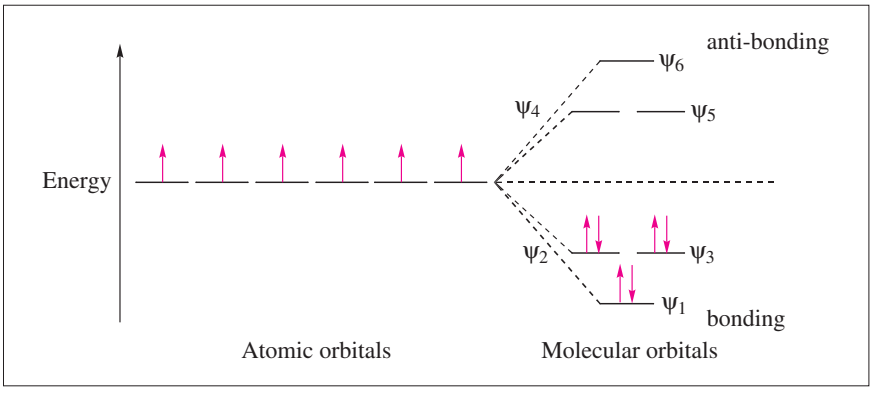


Figure 1.3

The double bond in but-1-ene, $CH_3CH_2CH{=}CH_2$, is fixed between C-1 and C-2; that is, it is localized. However, the double bonds in buta-1,3-diene, $CH_2{=}CH{-}CH{=}CH_2$ are not localized, but are spread over the whole molecule, and are said to be delocalized:

$$CH_2{=}CH{-}CH{=}CH_2$$

The same applies to the double bonds in benzene:

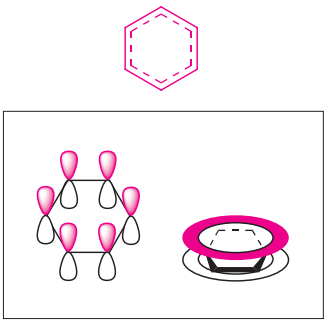
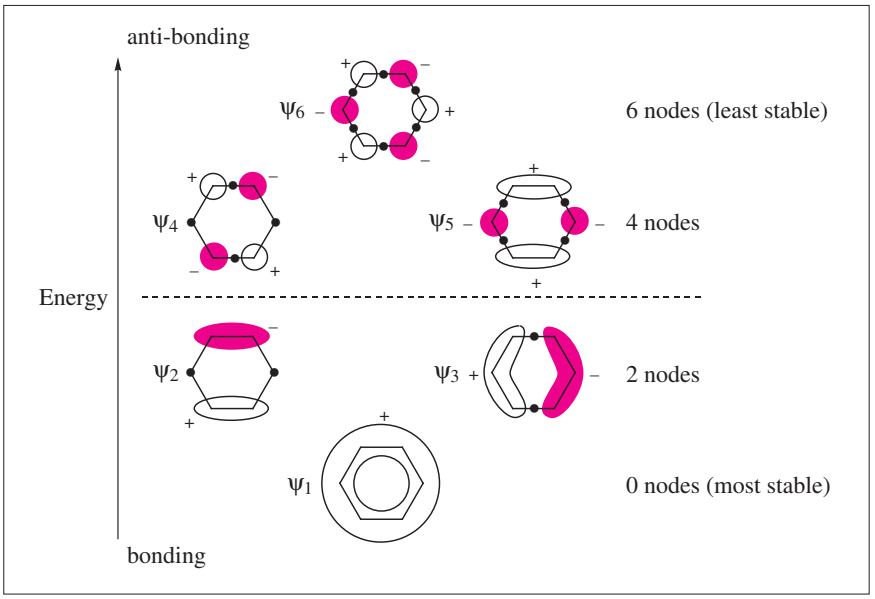


Figure 1.4

This arrangement accounts for the extra stability or aromaticity of benzene. The six overlapping p orbitals can be pictured as forming a **delocalized** π-electron cloud comprising of two rings (think of them as doughnuts!), one above and one below the molecular plane as shown in Figure 1.4. There are no localized C=C bonds as there are in alkenes.

The MOs of benzene are shown pictorially in Figure 1.5. The stability of a MO is related to the number of nodes it possesses; that is to say, the number of times the wave function changes phase (sign) around the ring system. The most stable form has no nodes, when there is a bonding interaction between all six adjacent carbon atoms.



A node is a point where the amplitude of a wave is zero:

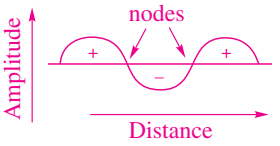


Figure 1.5

1.4 The Hückel Rule

It is important to examine aromaticity in its wider concept at this point. There are many compounds and systems besides benzene that are aromatic. They possess common features in addition to planarity and aromatic stability. MO calculations carried out by Hückel in the 1930s showed that aromatic character is associated with planar cyclic molecules that contained 2, 6, 10, 14 (and so on) π-electrons. This series of numbers is represented by the term $4n + 2$, where n is an integer, and gave rise to Hückel's $4n + 2$ rule that refers to the number of π-electrons in the p-orbital system. In the case of benzene, $n = 1$, and thus the system contains six π-electrons that are distributed in MOs as shown above.

Box 1.1 Hückel's Rule

A planar, cyclic system of unsaturated atoms containing $(4n + 2)$ π-electrons will be aromatic, where n is a positive integer or zero. It will possess extra stabilization. Some slight deviation from planarity is allowed. A similar system but containing $4n$ π-electrons will be **anti-aromatic**. Not only will it lack aromatic stabilization, but the closed loop of π-electrons will result in additional **destabilization** with respect to that anticipated.

These ideas are predicted by calculation and are confirmed by experiment.

This rule is now an important criterion for aromaticity. Those systems that contain $4n$ π-electrons are unstable and are referred to as anti-aromatic compounds.

Degenerate orbitals have equal energies.

The presence of electrons in anti-bonding orbitals is destabilizing. Orbitals that fall on the energy reference line are called nonbonding orbitals; the presence of electrons in these orbitals has no influence on the total bonding.

The reason for the success of the Hückel rule in predicting aromaticity lies in the derivation of the π MOs. For cyclic conjugated molecules, the energy levels of the bonding MOs are always arranged with one lowest-lying MO followed by degenerate pairs of orbitals. The anti-bonding orbitals are arranged inversely, with sets of two degenerate levels and a single highest energy orbital. In the case of benzene, it requires two electrons to fill the first MO and then four electrons to fill each of the n succeeding energy levels, as illustrated in Figure 1.3. A filled set of bonding MOs results in a stable system. This idea is very like that which links the stability of the noble gases to a filled set of atomic orbitals.

Worked Problem 1.1

Q Draw MO diagrams for the π-electron systems of cyclobutadiene and cyclooctatetraene.

A There is a simple system for predicting energy levels of MOs in cyclic systems. A polygon is inscribed within a circle with an apex at the base and horizontal lines are drawn at the points where the polygon touches the circle. The number of points of contact and their position determines the nature of the orbital and the relative energy. A non-bonding orbital results when the polygon touches the circle at a horizontal diameter. Touching below this line indicates bonding orbitals of lower energy; these are filled with electrons first, in accord with Hund's rule. Contact points above the horizontal diametric line correspond to higher energy anti-bonding orbitals. This is illustrated in Figure 1.6 for cyclobutadiene, benzene and cyclooctatetraene, having four, six, and eight carbon atoms, respectively. It can be seen that of these examples only benzene obeys Hückel's $4n + 2$ rule; both cyclobutadiene and cyclooctatetraene apparently have unpaired electrons. However, cyclooctatetraene is not planar, existing in a tub shape, and it behaves as a polyalkene with all the π-electrons paired up.

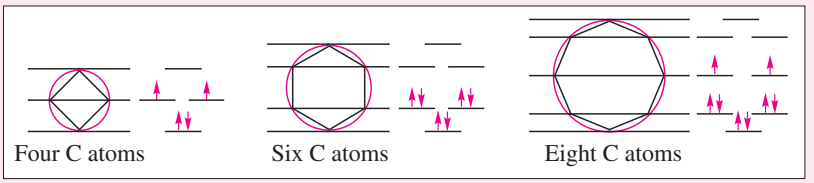


Figure 1.6

This method can also be used for other simple monocyclic systems that can be inscribed in a circle.

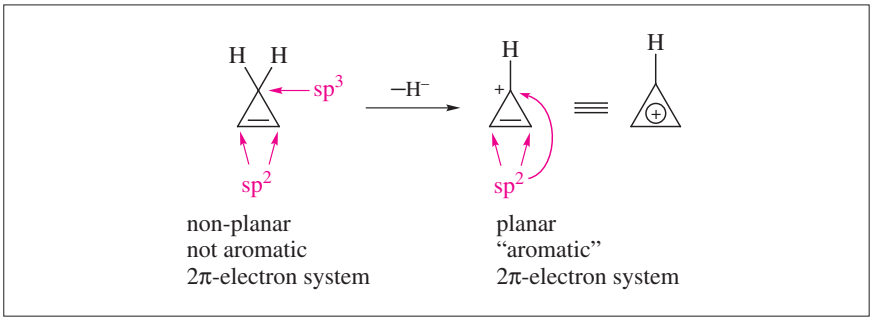
Although adherence to the Hückel rule is a valuable test for aromaticity, other properties are also used to assess whether a compound is aromatic or not. One such diagnostic tool is ^{1}H NMR spectroscopy. When exposed to a magnetic field, the π-electron cloud circulates to produce a ring current that generates a local magnetic field (Figure 1.7). This new field boosts the applied magnetic field outside the ring. As a result, the hydrogen atoms are deshielded and resonate at a lower applied field, usually in the range δ 6.5–8.5 ppm. Alkenyl hydrogen atoms are also deshielded, but to a lesser extent and normally resonate in the region δ 4.5–5.5 ppm. The local field inside the ring opposes the applied field and this effect is apparent in the ^{1}H NMR spectra of the annulenes (see p. 11).

The chemical shift of the resonance signal of a proton, δ_H, is measured relative to a standard, tetramethylsilane, $(CH_3)_4Si$, for which δ_H is 0.00 ppm. It reflects the chemical environment of the proton. A similar situation applies to the resonance signal δ_C for a ^{13}C nucleus.

Aromatic compounds also show characteristic infrared and ultraviolet absorption spectra. In the mass spectrum of aromatic substances, peaks corresponding to ions such as $C_6H_5^+$ and $C_6H_6^+$ are often seen. A commonly observed peak occurs at *m/z* 91, corresponding to the stable ion $C_6H_5CH_2^+$. These features are all helpful in assigning aromatic character.

1.4.1 2π-Electron Systems

Aromatic systems that obey Hückel's $4n + 2$ rule where $n = 0$ and so possess two π-electrons do exist and are indeed stable. The smallest possible ring is three membered and the derived unsaturated structure is cyclopropene. The theoretical loss of a hydride ion from this molecule leads to the cyclopropenyl cation, which contains two π-electrons distributed over the three carbon atoms of the planar cyclic system (Figure 1.8).



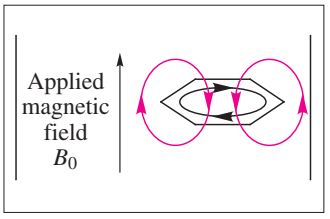
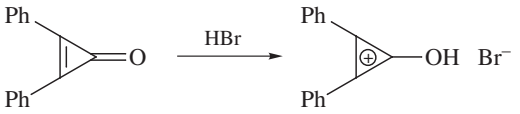


Figure 1.7

A circle with a charge inside it and inscribed within a ring structure is used to denote a $(4n + 2)$ π-electron system.

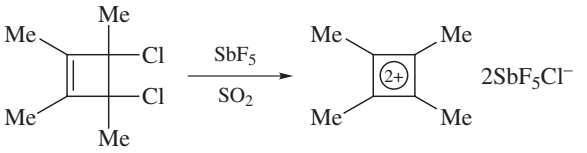
Figure 1.8

This cationic species and a number of its derivatives have been prepared and they are quite stable, despite the strain associated with the internal bond angles of only 60°. For example, the reaction of hydrogen bromide with diphenylcyclopropenone, which is itself a stable compound with aromatic character, gives the diphenylcyclopropenium salt (Scheme 1.1).



Scheme 1.1

Examination of the cyclobutadiene system indicates that it possesses four π-electrons and is thus an unstable 4*n* system. Cyclobutadiene itself only exists at very low temperatures, though some of its derivatives are stable to some extent at room temperature. Cyclobutadiene is a rectangular diene. Loss of two electrons through the departure of two chloride ions from the 3,4-dichlorocyclobutene derivative creates a 2π-electron aromatic system, the square, stable cyclobutenyl dication (Scheme 1.2).



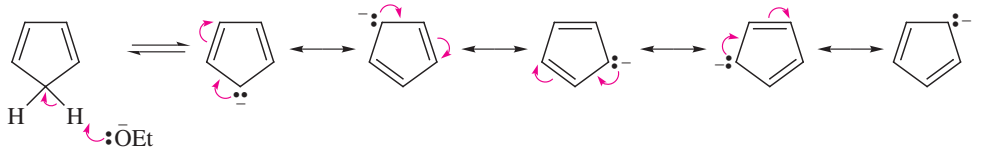
Scheme 1.2

1.4.2 6π-Electron Systems

We have seen that benzene fits into this category, but there are a number of other stable aromatic systems that contain six π-electrons.

Cyclopentadiene is surprisingly acidic (pK_a *ca.* 16) for a hydrocarbon. This property arises because the cyclopentadienyl anion, generated by abstraction of a proton by a base such as sodium ethoxide (Scheme 1.3), has a delocalized aromatic set of six π-electrons.

A curly (or curved) arrow, ↷, is used to show the movement of an electron pair.



Scheme 1.3

The cyclopentadienyl anion **13** is an efficiently **resonance-stabilized anion** in which all the carbon–carbon bond lengths are equal (Figure 1.9). It forms stable compounds, of which ferrocene (**14**) is an example, which undergo aromatic substitution reactions such as sulfonation and acetylation.

In contrast, it is the **resonance-stabilized cation** derived from cycloheptatriene that possesses the aromatic sextet of π-electrons. Tropylium bromide is formed by the addition of bromine to cycloheptatriene and

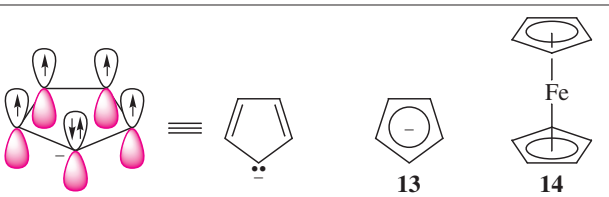
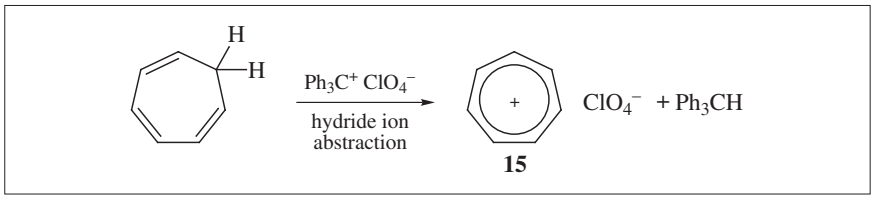


Figure 1.9

then loss of hydrogen bromide by heating. It can also be generated directly from cycloheptatriene by hydride ion abstraction using triphenylcarbenium perchlorate (Scheme 1.4). In the tropylium ion **15**, the bond lengths are equal and all seven carbon atoms share the positive charge (Figure 1.10).

Unlike cyclopentadiene, cycloheptatriene is not an acidic hydrocarbon; its pK_a is about 36. If a proton could be abstracted from cycloheptatriene, the resulting anion would have eight π-electrons and would be an unstable, anti-aromatic system.



Scheme 1.4

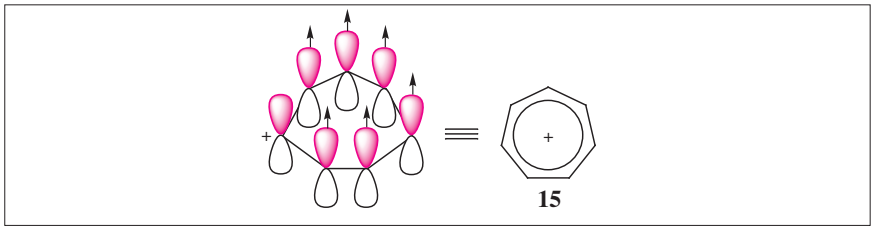
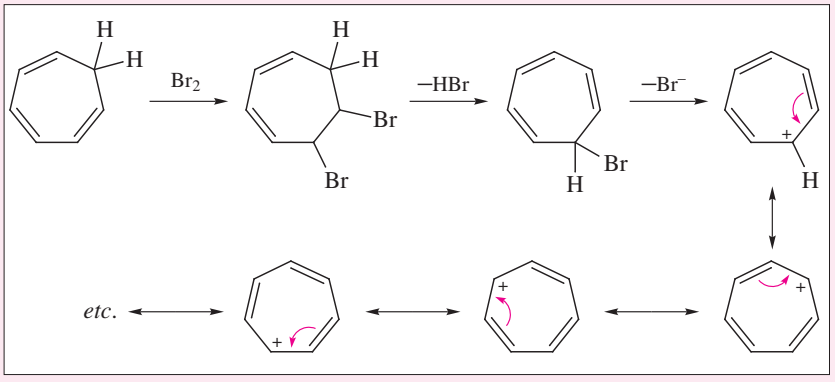


Figure 1.10

Worked Problem 1.2

Q Write an equation to show the formation of the cycloheptatrienyl cation by addition of bromine to the hydrocarbon. Use curly arrows to illustrate the stabilization of the cation.

A Bromine adds to one double bond of cycloheptatriene in exactly the same way as it does to ethene (although conjugate 1,4- and 1,6-addition may be the preferred mode of reaction). Dehydrobromination occurs on heating. The driving force for the loss of bromide ion is the extra stability of the resulting cation. The positive charge is delocalized over the whole system (Scheme 1.5).



Scheme 1.5

A dipole moment is associated with a permanent uneven sharing of electron density in a molecule. It is a vector quantity that depends on the size of the partial charges in the molecule and the distance between them, and is measured in units of Debye (D). For example, chlorobenzene has a dipole moment of 1.75 D, oriented towards the chlorine. In 1,4-dichlorobenzene, the individual moments directed towards the chlorine atoms are equal and opposed to each other. Consequently, the dipole moment of this molecule is zero.

Azulene (**16**) is a stable, blue solid hydrocarbon that undergoes typical electrophilic aromatic substitution reactions. It may be regarded as a combination of **13** and **15**; in keeping with this it has a dipole moment of 0.8 D (Figure 1.11). The fusion bond linking the two rings is longer (150 pm) than the other bonds (139–140 pm), indicating that azulene is a peripherally conjugated system.

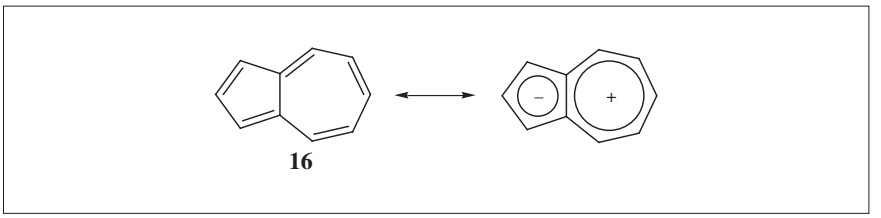


Figure 1.11

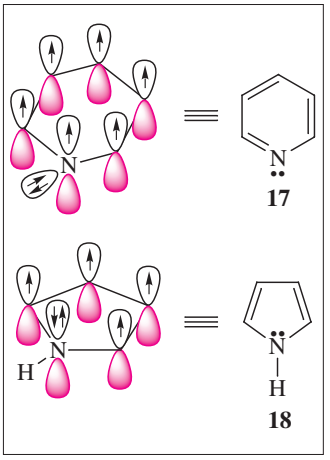


Figure 1.12

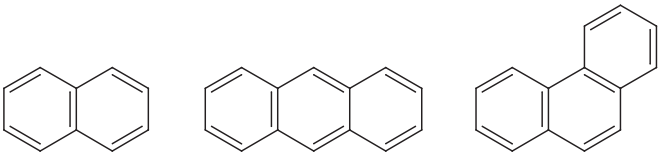
Addition of two electrons to cyclooctatetraene would lead to a 10π-electron system, the cyclooctatetraenyl dianion. Cyclooctatetraene, which is non-planar, reacts with potassium in tetrahydrofuran to give dipotassium cyclooctatetraenide, which is planar. The C–C bond lengths are all the same (141 pm). At low temperatures, a dication is formed when cyclooctatetraene reacts with SbF_5. This also has some aromatic characteristics in keeping with a 6π-electron system.

Some heterocyclic compounds possess aromatic character. One such important compound is pyridine (**17**), in which one of the CH units of benzene has been replaced by a nitrogen atom (Figure 1.12). Although the chemistry of pyridine shows several important differences from benzene, it also has some common characteristics. The five carbon atoms and the nitrogen atom each provide one electron for the π-cloud, thereby conferring aromaticity on pyridine according to Hückel's rule. Notice that the nitrogen retains a lone pair of electrons in an sp^2 orbital directed away from the ring; this accounts for the basic properties of pyridine.

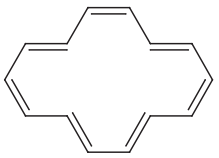
Similarly, the five-membered heterocycle pyrrole (**18**) is aromatic, although this molecule obeys Hückel's rule only because the nitrogen atom contributes two electrons to the π-cloud. In this respect, pyrrole is analogous to the cyclopentadienyl anion. As a consequence, the nitrogen atom does not retain a lone pair of electrons and pyrrole is not basic.

1.4.3 10π-, 14π- and 18π-Electron Systems

The most important 10π carbocyclic system is naphthalene (**19**) in which two benzene rings are fused together. The fused systems anthracene (**20**) and phenanthrene (**21**) obey Hückel's rule, where $n = 3$, and have 14π-electrons. All three compounds are typically aromatic and their chemistry is similar to that of benzene, as discussed in Chapter 12.



In 1962, Sondheimer prepared a series of conjugated monocyclic polyenes called **annulenes**, with the specific purpose of testing Hückel's rule. Amongst the annulenes prepared, compound **22** with 14 and compound **23** with 18 carbon atoms, that is n =3 and n = 4, respectively, have the magnetic properties required for aromatic character, but behave chemically like conjugated alkenes. In [18]annulene (**23**), the hydrogen atoms on the outside of the ring resonate in the aromatic region at δ 9.3 ppm. However, the inner protons lie in the region where the induced field associated with the ring current opposes the applied field. They are therefore shielded and so resonate upfield at δ –3.0 ppm.



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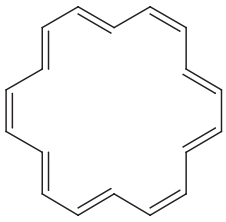

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1.5 Nomenclature

The remainder of this book will be devoted to the synthesis and reactions of a range of aromatic compounds. It is important that you understand the naming of these compounds. The use of trivial names is widespread, particularly in the chemical industry; although some of the older names have disappeared from use, many persist and are allowed in the IUPAC system. Some of these are presented in Figure 1.13.

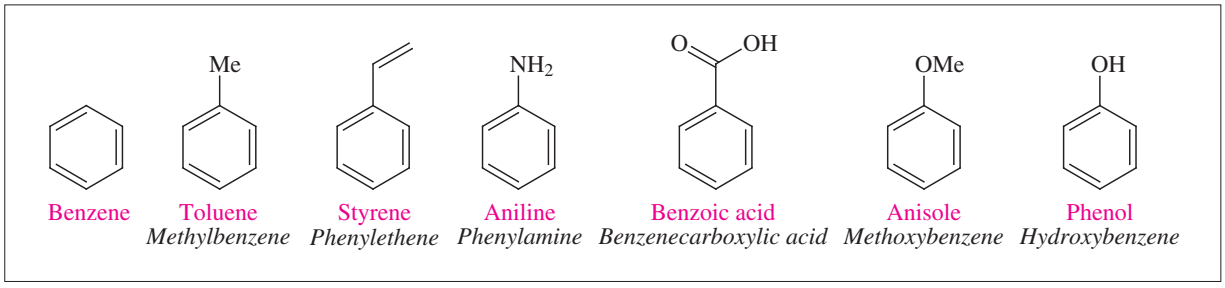


Figure 1.13

Monosubstituted compounds are commonly named as in aliphatic chemistry, with the substituents appearing as a prefix to the parent name benzene; bromobenzene, chlorobenzene and nitrobenzene are examples (Figure 1.14).

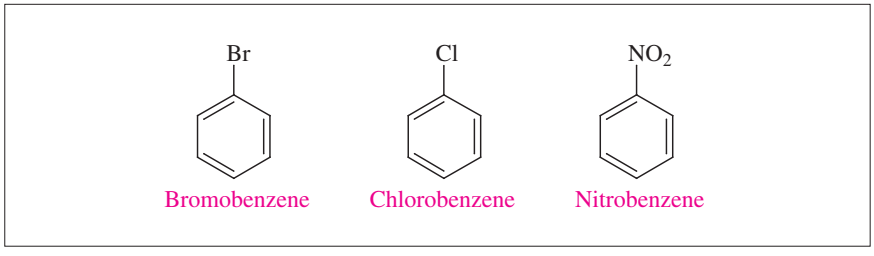
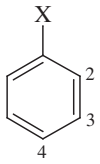


Figure 1.14

There are two acceptable ways of naming the three positional isomers that are possible for disubstituted benzene rings. The substituent



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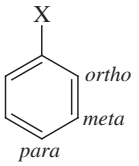

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positions 1,2-, 1,3- and 1,4- are sometimes replaced by the terms *ortho*-, *meta*- and *para*- (abbreviated to *o*-, *m*- and *p*-, respectively) (see **24** and **25**). You are advised to become familiar with both systems so that you can use them interchangeably.

In multiply substituted compounds, the groups are numbered so that the lowest possible numbers are used. The substituents are then listed in alphabetical order with their appropriate numbers. Examples are given in Figure 1.15, which also introduces further trivial names.

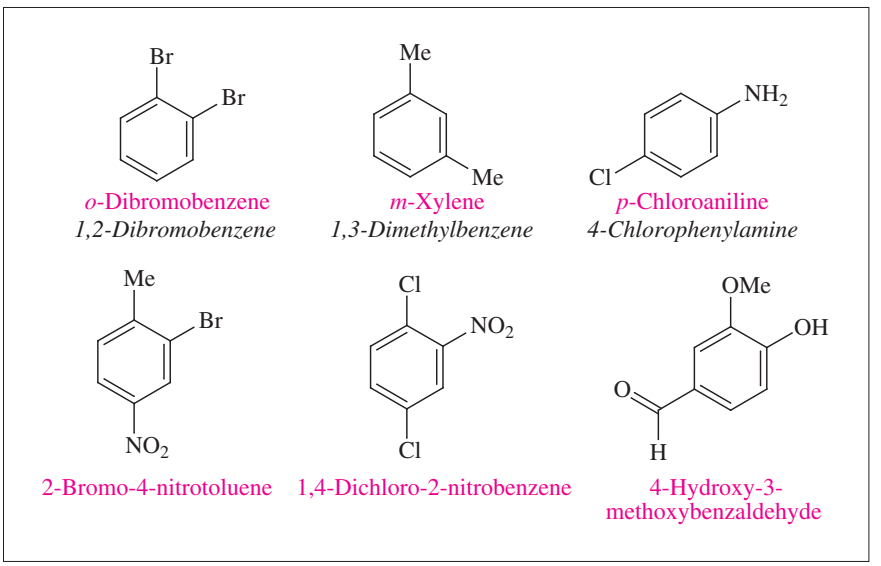


Figure 1.15

There are occasions when the benzene ring is named as a substituent and in these cases the name for C_6H_5- is phenyl, abbreviated to Ph. The name for $C_6H_5CH_2$- is benzyl or Bn, whilst the benzoyl substituent is C_6H_5CO- or Bz. These substituents can also be named systematically as shown in Figure 1.16.

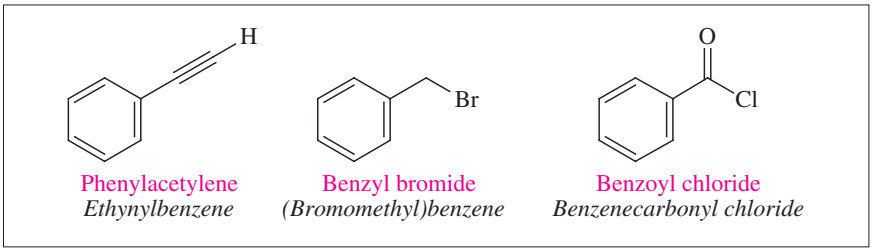


Figure 1.16

Summary of Key Points

1. Benzene is an unusually stable molecule. This aromatic stabilization is associated with its 6π-electron system.

2. Other molecules besides benzenoid compounds also show increased stability.

3. Aromatic stability is found in planar, cyclic conjugated systems that satisfy the Hückel rule in possessing $(4n + 2)$ π-electrons.

4. $(4n + 2)$ π-electrons corresponds to a completely filled set of bonding molecular orbitals.

5. Ionic species that comply with all the requirements for aromaticity are best regarded as resonance-stabilized ions.

6. Protons in an aromatic environment usually resonate at δ 6.5–8.5 ppm.

7. Cyclic, planar molecules with $4n$ π-electrons are particularly unstable and are said to be anti-aromatic.

8. Substitution reactions, which are the most important type shown by aromatic compounds, conserve aromatic stability.

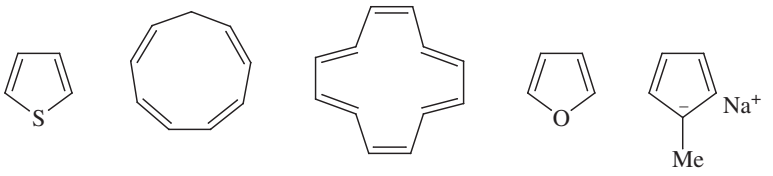
9. Addition reactions, which are less common, destroy the aromatic system.

Problems

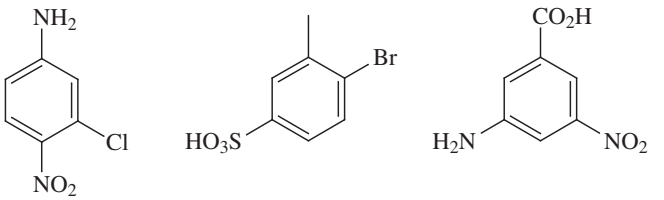
1.1. Draw the MO diagrams of the π-electron system for the following species: the cyclopropenyl radical, the cyclopropenyl cation, the cyclobutadienyl cation, the cyclopentadienyl anion, the tropylium cation, the cyclooctatetraenyl dication.

1.2. Cyclopropenones are described as having aromatic character. How would you account for this, given that the ring contains three π-electrons?

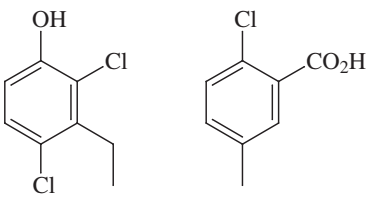
1.3. Which of the following compounds would you expect to be aromatic:



1.4. Give the systematic names for the following compounds:



(a) (b) (c)



(d) (e)

1.5. Draw structures for the following compounds: (a) 4-chloro-3-nitrobenzoic acid; (b) *m*-nitroethylbenzene; (c) 2,6-dibromo-4-nitroaniline; (d) *p*-chlorobenzenesulfonic acid; (e) *o*-nitrobenzaldehyde