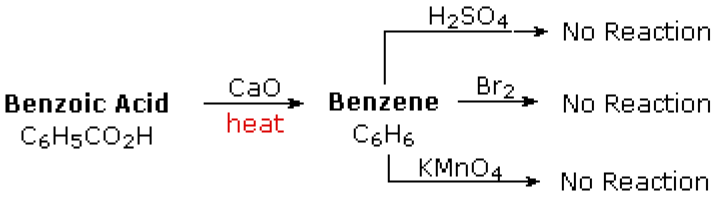
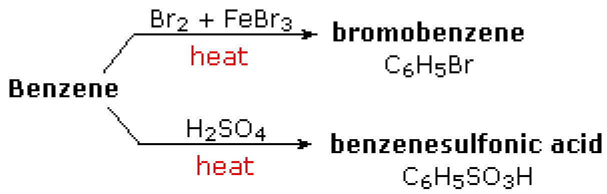
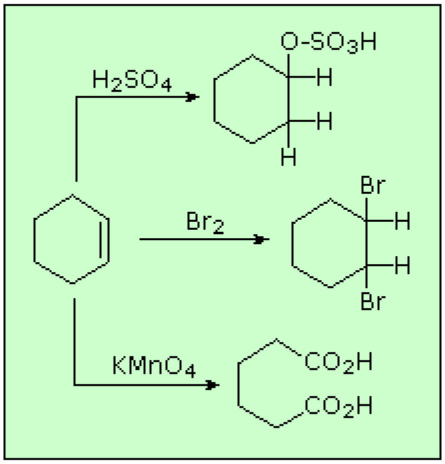
Benzene and Other Aromatic Compounds

The adjective "aromatic" is used by organic chemists in a rather different way than it is normally applied. It has its origin in the observation that certain natural substances, such as cinnamon bark, wintergreen leaves, vanilla beans and anise seeds, contained fragrant compounds having common but unexpected properties. Cinnamon bark, for example, yielded a pleasant smelling compound, formula C_9H_8O, named cinnamaldehyde. Because of the low hydrogen to carbon ratio in this and other aromatic compounds (note that the H:C ratio in an alkane is >2), chemists expected their structural formulas would contain a large number of double or triple bonds. Since double bonds are easily cleaved by oxidative reagents such as potassium permanganate or ozone, and rapidly add bromine and chlorine, these reactions were applied to these aromatic compounds. Surprisingly, products that appeared to retain many of the double bonds were obtained, and these compounds exhibited a high degree of chemical stability compared with known alkenes and cycloalkenes (aliphatic compounds). On treatment with hot permanganate solution, cinnamaldehyde gave a stable, crystalline $C_7H_6O_2$ compound, now called benzoic acid. The H:C ratio in benzoic acid is <1, again suggesting the presence of several double bonds. Benzoic acid was eventually converted to the stable hydrocarbon benzene, C_6H_6, which also proved unreactive to common double bond transformations, as shown below. For comparison, reactions of cyclohexene, a typical alkene, with these reagents are also shown (green box). As experimental evidence for a wide assortment of compounds was acquired, those incorporating this exceptionally stable six-carbon core came to be called "aromatic".

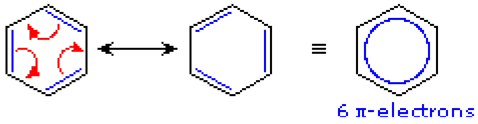






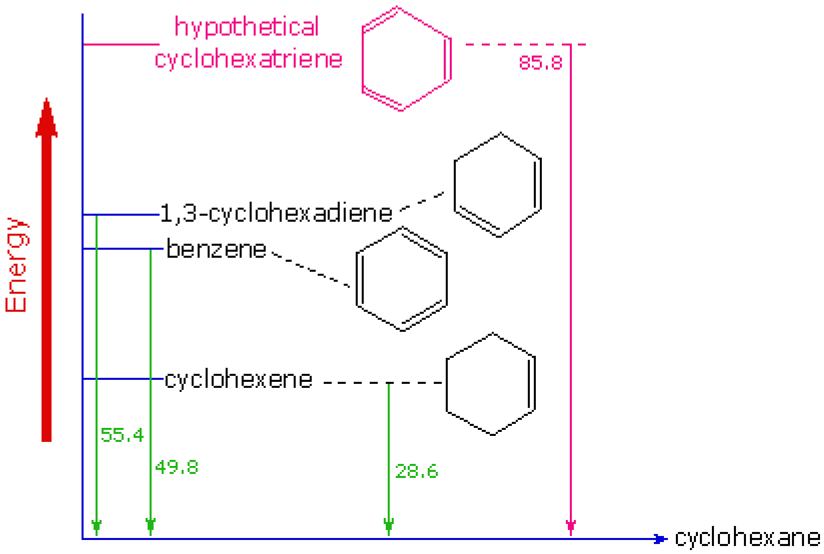
If benzene is forced to react by increasing the temperature and/or by addition of a catalyst, It undergoes **substitution reactions** rather than the addition reactions that are typical of alkenes. This further confirms the previous indication that the six-carbon benzene core is unusually stable to chemical modification. The conceptual contradiction presented by a high degree of unsaturation (low H:C ratio) and high chemical stability for benzene and related compounds remained an unsolved puzzle for many years. Eventually, the presently accepted structure of a regular-hexagonal, planar ring of carbons was adopted, and the exceptional thermodynamic and chemical stability of this system was attributed to resonance stabilization of a conjugated cyclic triene.

Benzene:

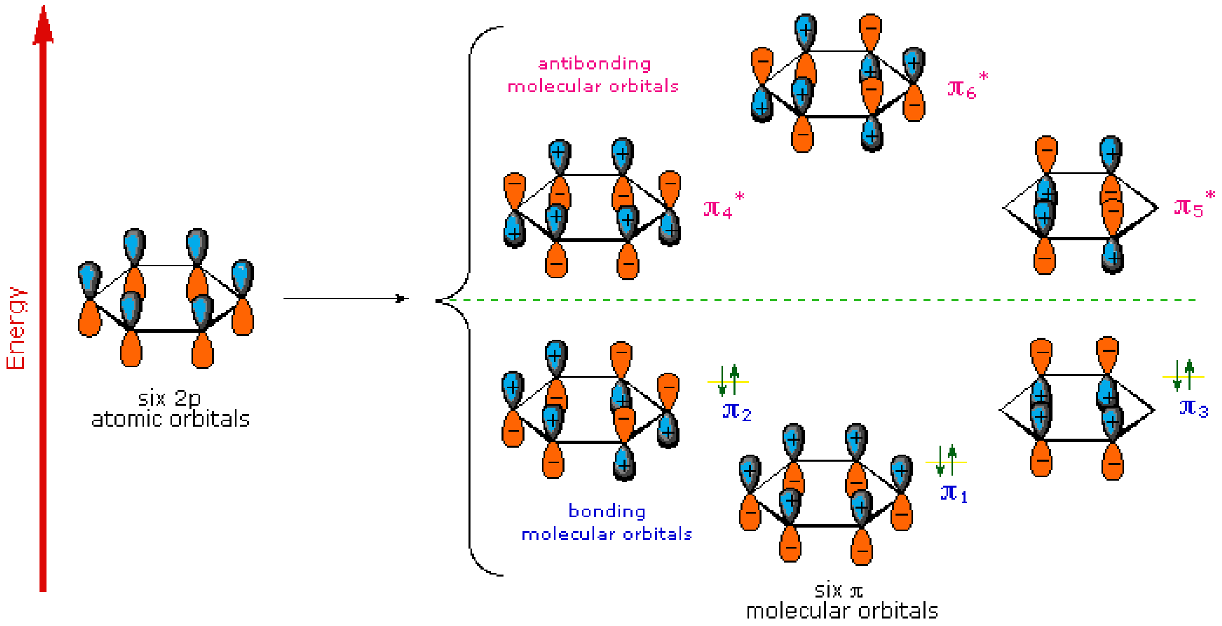


Here, two structurally and energetically equivalent electronic structures for a stable compound are written, but no single structure provides an accurate or even an adequate representation of the true molecule. The six-membered ring in benzene is a perfect hexagon (all carbon-carbon bonds have an identical length of 1.40 Å). The cyclohexatriene contributors would be expected to show alternating bond lengths, the double bonds being shorter (1.34 Å) than the single bonds (1.54 Å). An alternative representation for benzene (circle within a hexagon) emphasizes the pi-electron delocalization in this molecule, and has the advantage of being a single diagram. In cases such as these, the electron delocalization described by resonance enhances the stability of the molecules, and compounds composed of such molecules often show exceptional stability and related properties.

Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product. In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 28.6 kcal per mole. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 57.2 kcal per mole on complete hydrogenation, and 1,3,5-cyclohexatriene to release 85.8 kcal per mole. These **heats of hydrogenation** would reflect the relative thermodynamic stability of the compounds. In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 2 kcal, presumably due to conjugation of the double bonds. **Benzene, however, is an extraordinary 36 kcal/mole more stable than expected**. This sort of stability enhancement is now accepted as a characteristic of all aromatic compounds.



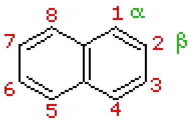
A molecular orbital description of benzene provides a more satisfying and more general treatment of "aromaticity". We know that benzene has a planar hexagonal structure in which all the carbon atoms are sp^2 hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding. The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals (in the diagram the phases are also color coded). When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g. π_1) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals. It is this completely filled set of bonding orbitals, or **closed shell**, that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases.



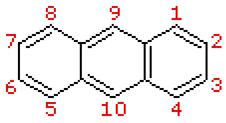
The Molecular Orbitals of Benzene

Fused Benzene Ring Compounds

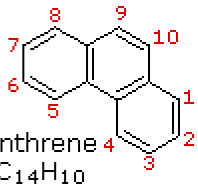
Benzene rings may be joined together (fused) to give larger polycyclic aromatic compounds. A few examples are drawn below, together with the approved numbering scheme for substituted derivatives. The peripheral carbon atoms (numbered in all but the last three examples) are all bonded to hydrogen atoms. Unlike benzene, all the C-C bond lengths in these fused ring aromatics are not the same, and there is some localization of the pi-electrons. For a discussion of this characteristic in cases of naphthalene and phenanthrene click on their formulas.
The six benzene rings in coronene are fused in a planar ring; whereas the six rings in hexahelicene are not joined in a larger ring, but assume a helical turn, due to the crowding together of the terminal ring atoms. This helical configuration renders the hexahelicene molecule chiral, and it has been resolved into stable enantiomers having specific rotations of 3700º. Models of corannulene, coronene and hexahelicene may be examined by clicking on the appropriate structure in the diagram.



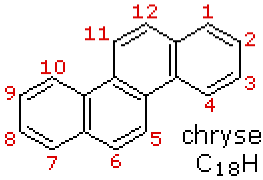
naphthalene
$C_{10}H_8$
m.p. 81° C



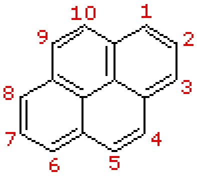
anthracene
$C_{14}H_{10}$
m.p. 217° C



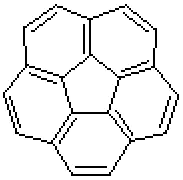
phenanthrene
$C_{14}H_{10}$
m.p. 100° C



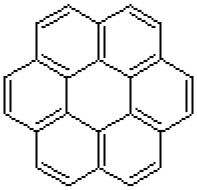
chrysene
$C_{18}H_{12}$
m.p. 253° C



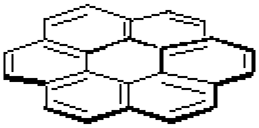
pyrene
$C_{16}H_{10}$
m.p. 150° C



corannulene
$C_{20}H_{10}$
m.p. 268° C



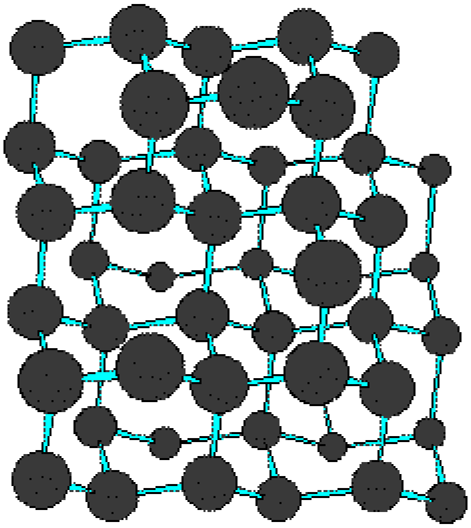
coronene
$C_{24}H_{12}$
m.p. 442° C



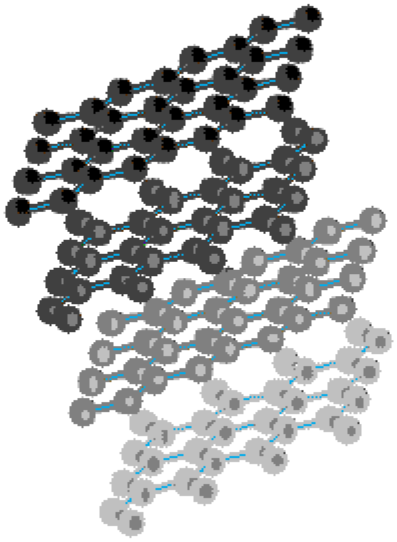
hexahelicene
$C_{26}H_{16}$
m.p. 230° C

As these extended aromatic compounds become larger, the ratio of hydrogen to carbon decreases. For example, the symmetrical hexacyclic compound coronene has a H/C ratio =1/2, compared with 1 for benzene. If we were to imagine fused ring systems of this kind to be further extended in space, the H/C ratio would approach zero, and the resulting compound would be a form of carbon. Such a carbon allotrope exists and is called **graphite**. Another well-characterized carbon allotrope is **diamond**. The structures for these two forms of carbon are very different, and are displayed below. Diamond is an extended array of sp^3 hybridized carbon atoms; whereas, graphite consists of overlapping sheets of sp^2 hybridized carbon atoms arranged in a hexagonal pattern. You may examine models of partial diamond and graphite structures by clicking on the appropriate structure below.

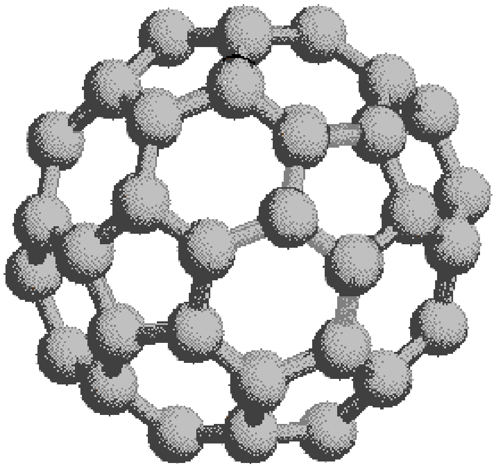
Diamond



Graphite

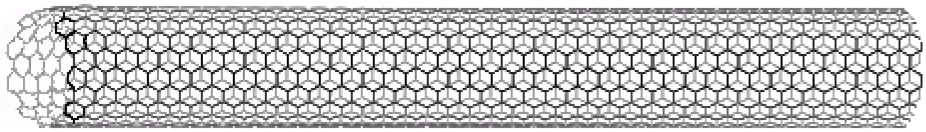


A comparison of the coronene and corannulene models discloses an interesting difference in their shapes. Coronene is absolutely flat and, aside from the peripheral hydrogens, resembles a layer of graphite. Its very high melting point reflects this resemblance. Corannulene, on the other hand, is slightly curved, resulting in a bowl-like shape.



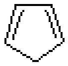
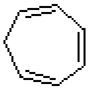
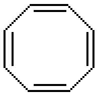
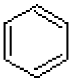
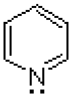
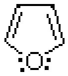
If we extend the structure of corannulene by adding similar cycles of five benzene rings, the curvature of the resulting molecule should increase, and eventually close into a sphere of carbon atoms. The archetypical compound of this kind (C_{60}) has been named **buckminsterfullerene** because of its resemblance to the geodesic structures created by Buckminster Fuller. It is a member of a family of similar carbon structures that are called **fullerenes**. These materials represent a third class of carbon allotropes. Alternating views of the C_{60} fullerene structure are shown on the right, together with a soccer ball-like representation of the 12 five and 20 six-membered rings composing its surface. Precise measurement by Atomic Force Microscopy (AFM) has shown that the C-C bond lengths of the six-membered rings are not all equal, and depend on whether the ring is fused to a five or six-membered beighbor. By clicking on this graphic, a model of C_{60} will be displayed.
Although C_{60} is composed of fused benzene rings its chemical reactivity resembles that of the cycloalkenes more than benzene. Indeed, exposure to light and oxygen slowly degrade fullerenes to cage opened products. Most of the reactions thus far reported for C_{60} involve addition to, rather than substitution of, the core structure. These reactions include hydrogenation, bromination and hydroxylation. Strain introduced by the curvature of the surface may be responsible for the enhanced reactivity of C_{60}. . Larger fullerenes, such as C_{70}, C_{76}, C_{82} & C_{84}have ellipsoidal or distorted spherical structures, and fullerene-like assemblies up to C_{240} have been detected. A model of the C_{70} fullerene may be examined by clicking here. A fascinating aspect of these structures is that the space within the carbon cage may hold atoms, ions or small molecules. Such species are called **endohedral fullerenes**. The cavity of C_{60} is relatively small, but encapsulated helium, lithium and atomic nitrogen compounds have been observed. Larger fullerenes are found to encapsulate lanthanide metal atoms.

Interest in the fullerenes has led to the discovery of a related group of carbon structures referred to as nanotubes. As shown in the following illustration, nanotubes may be viewed as rolled up segments of graphite. The chief structural components are six-membered rings, but changes in tube diameter, branching into side tubes and the capping of tube ends is accomplished by fusion with five and seven-membered rings. Many interesting applications of these unusual structures have been proposed.



Other Aromatic Systems

Many unsaturated cyclic compounds have exceptional properties that we now consider characteristic of "aromatic" systems. The following cases are illustrative:

Compound	**Structural Formula**	**Reaction with Br_2**	**Thermodynamic Stabilization**
1,3-Cyclopentadiene		Addition (0 ºC)	Slight
1,3,5-Cycloheptatriene		Addition (0 ºC)	Slight
1,3,5,7-Cyclooctatetraene		Addition (0 ºC)	Slight
Benzene		Substitution	Large
Pyridine		Substitution	Large
Furan		Substitution (0 ºC)	Moderate
Pyrrole		Substitution	Moderate

The first three compounds (cyclic polyenes) have properties associated with alkenes in general. Each reacts readily with bromine to give addition products, as do most alkenes. The thermodynamic change on introducing double bonds into the carbon atom ring is also typical of alkenes (a destabilization of ca. 26 kcal/mol for each double bond). Conjugation offsets this increase in energy by a small amount (4-6 kcal/mol).

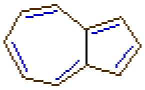
The remaining four compounds exhibit very different properties, and are considered aromatic. Benzene and pyridine are relatively unreactive with bromine, requiring heat and/or catalysts to force reaction, the result of which is substitution rather than addition. Furan and pyrrole react more rapidly with bromine, but they also give substitution products. This tendency to favor substitution rather than addition suggests that the parent unsaturated ring system has exceptional stability. Thermodynamic measurements support this conclusion. The enhanced stability, often referred to as **aromatic stabilization**, ranges (in the above cases) from a low of 16 kcal/mol for furan to 36 kcal/mol for benzene.

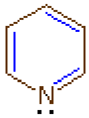
Factors Required for Aromaticity

- A planar (or near planar) cycle of sp^2 hybridized atoms, the p-orbitals of which are oriented parallel to each other. These overlapping p-orbitals generate an array of π-molecular orbitals.
- These π-orbitals are occupied by 4n+2 electrons (where n is an integer or zero). This requirement is known as **The Hückel Rule**. All the aromatic compounds discussed above have 6 π-electrons (n=1).

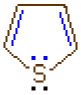
1,3-Cyclopentadiene and 1,3,5-cycloheptatriene both fail to meet the first requirement, since one carbon atom of each ring is sp^3 hybridized and has no p-orbital. Cyclooctatetraene fails both requirements, although it has a ring of sp^2 hybridized atoms. This molecule is not planar (a geometry that would have 135º bond angles). Angle strain is relieved by adopting a tub-shaped conformation; consequently, the p-orbitals can only overlap as isolated pairs, not over the entire ring. Furthermore, cyclooctatetraene has 8 π-electrons, a number not consistent with the Hückel Rule.

Benzene is the archetypical aromatic compound. It is planar, bond angles=120º, all carbon atoms in the ring are sp^2 hybridized, and the pi-orbitals are occupied by 6 electrons. The aromatic heterocycle pyridine is similar to benzene, and is often used as a weak base for scavenging protons. Furan and pyrrole have heterocyclic five-membered rings, in which the heteroatom has at least one pair of non-bonding valence shell electrons. By hybridizing this heteroatom to a sp^2 state, a p-orbital occupied by a pair of electrons and oriented parallel to the carbon p-orbitals is created. The resulting planar ring meets the first requirement for aromaticity, and the π-system is occupied by 6 electrons, 4 from the two double bonds and 2 from the heteroatom, thus satisfying the Hückel Rule.

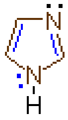

azulene



pyridine



thiophene



imidazole

Four illustrative examples of aromatic compounds are shown above. The sp^2 hybridized ring atoms are connected by brown bonds, the π-electron pairs and bonds that constitute the aromatic ring are colored blue. Electron pairs that are not part of the aromatic π-electron system are black. The first example is azulene, a blue-colored 10 π-electron aromatic hydrocarbon isomeric with naphthalene. The second and third compounds are heterocycles having aromatic properties. Pyridine has a benzene-like six-membered ring incorporating one nitrogen atom. The non-bonding electron pair on the nitrogen is not part of the aromatic π-electron sextet, and may bond to a proton or other electrophile without disrupting the aromatic system. In the case of thiophene, a sulfur analog of furan, one of the sulfur electron pairs (colored blue) participates in the aromatic ring π-electron conjugation. The last compound is imidazole, a heterocycle having two nitrogen atoms. Note that only one of the nitrogen non-bonding electron pairs is used for the aromatic π-electron sextet. The other electron pair (colored black) behaves similarly to the electron pair in pyridine.

Source : http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/react3.htm#rx10