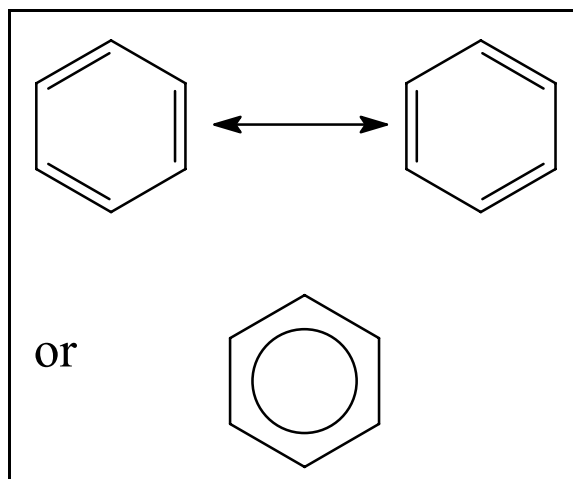# BENZENE - AROMATIC COMPOUNDS

Aliphatic Compounds: Open chain (acyclic) and those cyclic compounds with similar chemical properties. A typical reaction type of unsaturated aliphatic compounds: electrophilic addition.

Aromatic Compounds: Benzene, C_6H_6, and other unsaturated compounds that resemble it in chemical behavior. The aromatic properties of benzene are those that distinguish it from aliphatic hydrocarbons.

Benzene

What are these properties?

Properties of Aromatic Compounds ---

☞   Cyclic and each atom in the ring is a π-center (uses a p atomic orbital to form π-type bonds),
      ie, sp^2 or sp.

☞   Ring is flat or nearly so.

☞ High degree of unsaturation but resistant to addition reactions --- generally undergo electrophilic *substitution* (an electrophilic reagent replaces a hydrogen [usually] attached to the ring).

☞ Unusually stable.

☞ π-Electrons delocalized above and below plane of ring.

Benzene Molecular Orbitals

σ-Orbitals —

Each carbon is sp^2 hybridized. The 18 carbon sp^2 atomic orbitals [(3/carbon)x(6 carbons)] and 6 hydrogen s atomic orbitals interact to form 12 σ and 12 σ* molecular orbitals. The 24 electrons from the atomic orbitals occupy the 12 σ orbitals giving 12 σ bonds.
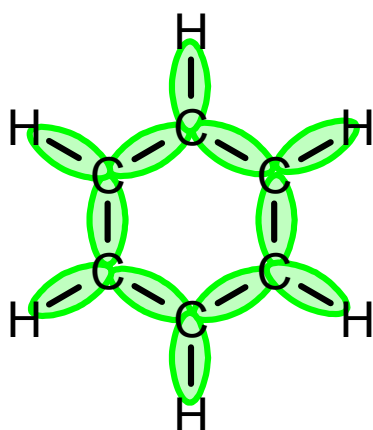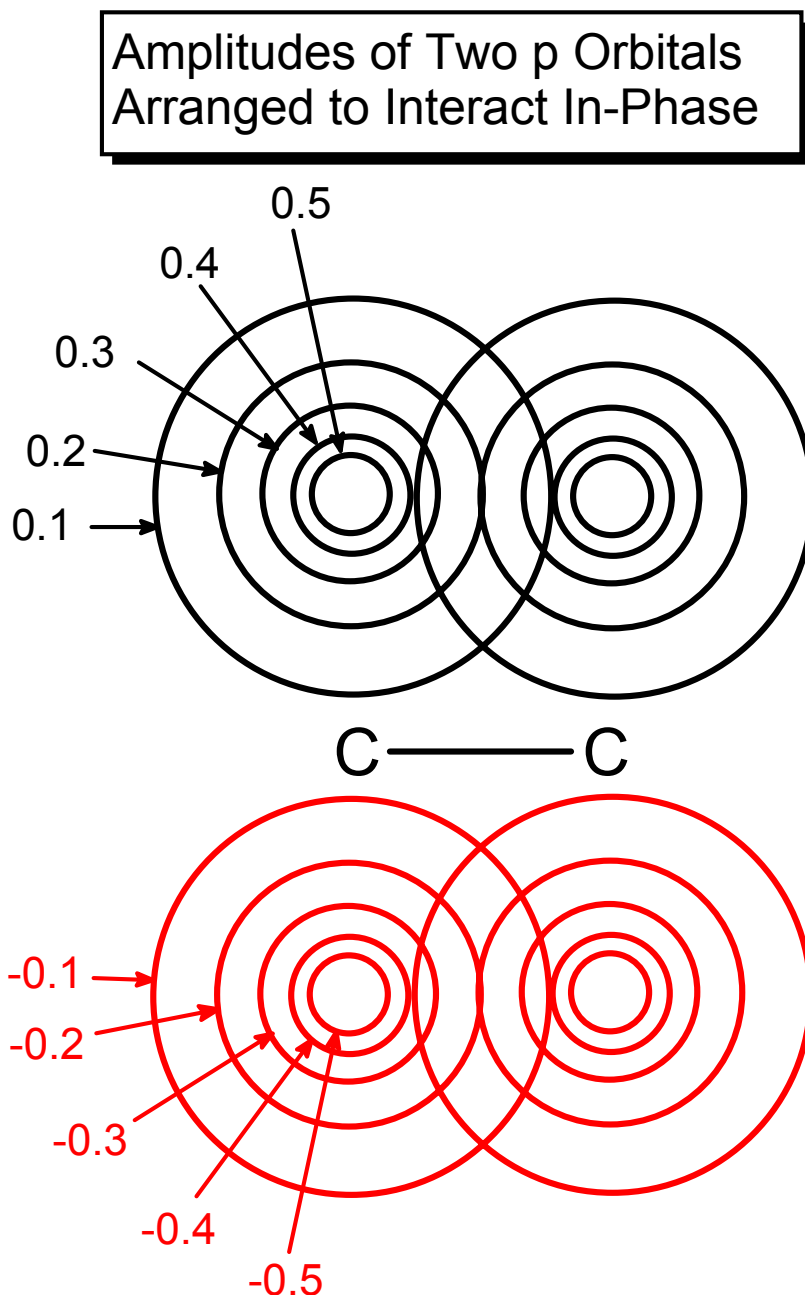

= a σ-orbital; containing 2 electrons, a σ-bond

π-Orbitals —

π-Type orbitals form by the parallel overlap of p atomic orbitals.

P orbitals have two lobes. One lobe has a positive amplitude and the other a negative amplitude – metaphorically, a hill and a valley. If two adjacent p orbitals are in phase – hill next to hill and valley next to valley – they will overlap to form a molecular orbital in a constructive way: one hill will join with the other and one valley will join with the other. Electrons will be found wherever the amplitude ≠ 0. This situation – bonding – is shown in the figure to the right.

Amplitudes of Two p Orbitals Arranged to Interact In-Phase

0.5
0.4
0.3
0.2
0.1

C———C

-0.1
-0.2
-0.3
-0.4
-0.5

On the other hand, if two adjacent p orbitals are out of phase – hill next to valley and valley next to hill – they will overlap in a destructive way: the hills and valleys will be leveled and in some places the amplitude will be zero. [The places where the amplitude is 0 is called a *node*.] Electrons are not found at nodes. This situation – antibonding – is shown in the figure to the right.

Amplitudes of Two p Orbitals Arranged to Interact Out-Of-Phase

0.5
0.4
0.3
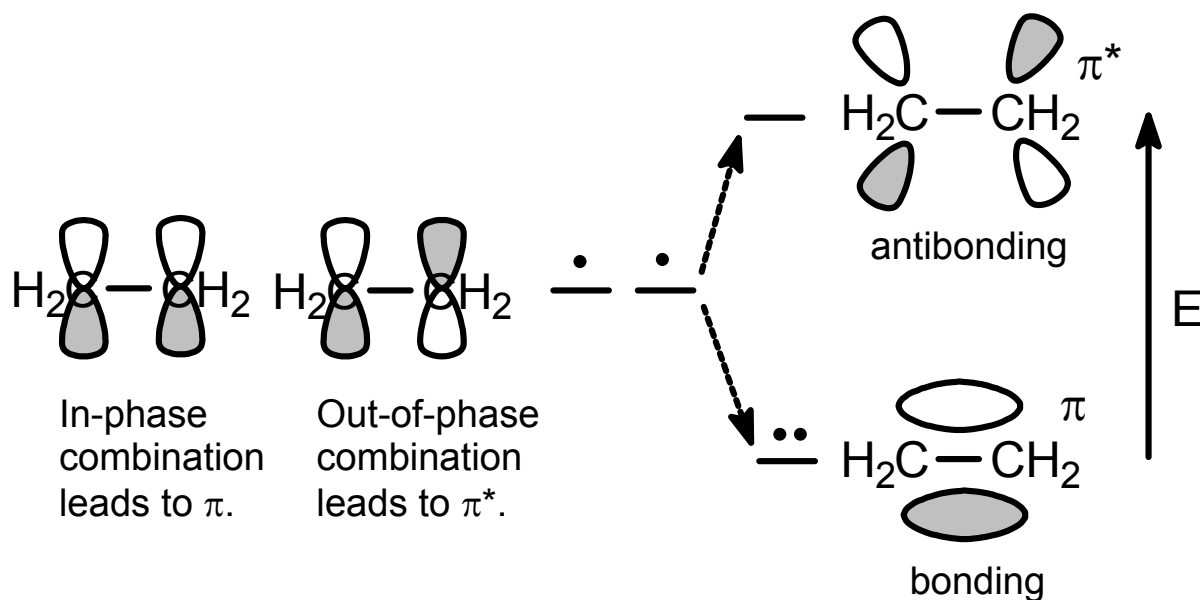0.2
0.1

Node

C————C

-0.1
-0.2
-0.3
-0.4
-0.5
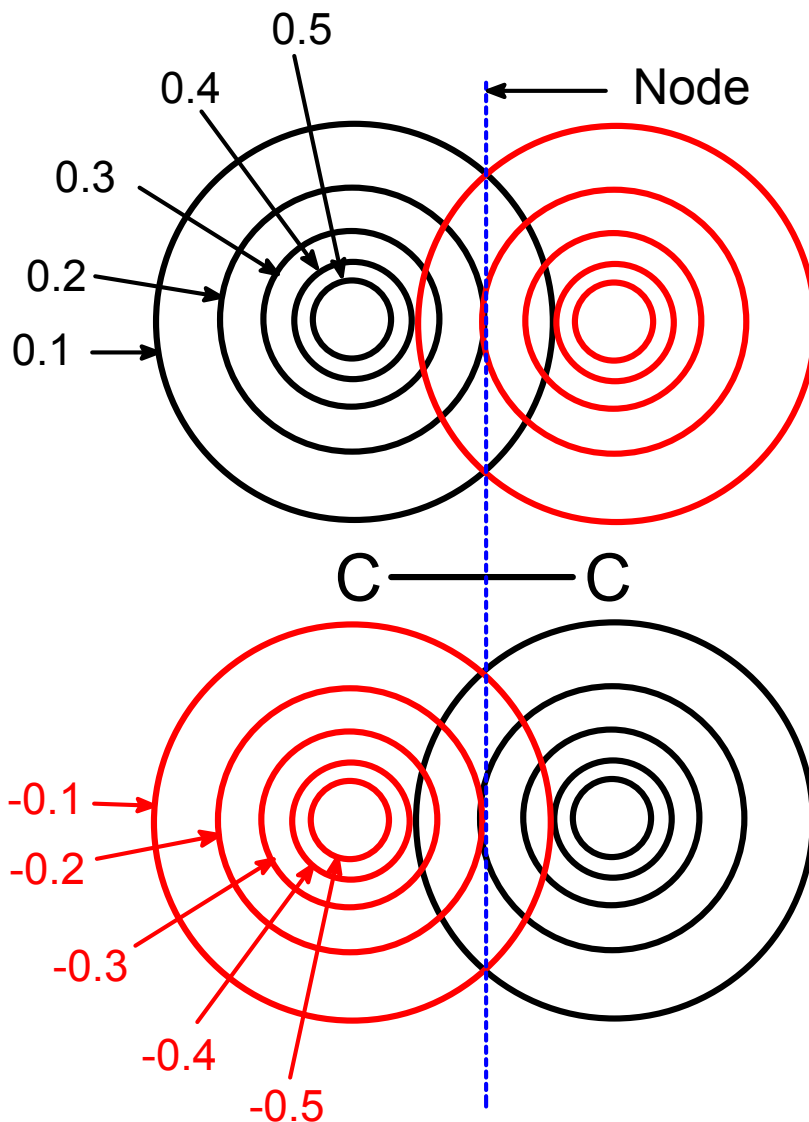
Finally, it sometimes happens that the p orbital of a particular atom contributes nothing to a molecular orbital. The amplitude of the molecular orbital at that atom is zero. This is a nonbonding situation for that molecular orbital for that atom.

Before we consider benzene, let's look at a couple of simpler compounds (which happen to be aliphatic) that have π-bonds.
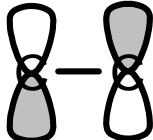
<u>Ethylene</u>

The π and π^* orbitals in ethylene are formed by a combining of the 2p atomic orbitals of the carbons. The π orbital is bonding between the two carbons – electrons in this orbital have less energy than they would have in an atomic 2p orbital. The π^* orbital is antibonding – electrons in this orbital have more energy than they would have in an atomic 2p orbital.

In-phase combination leads to π.

Out-of-phase combination leads to π^*.

π^*

$H_2C - CH_2$

antibonding

π
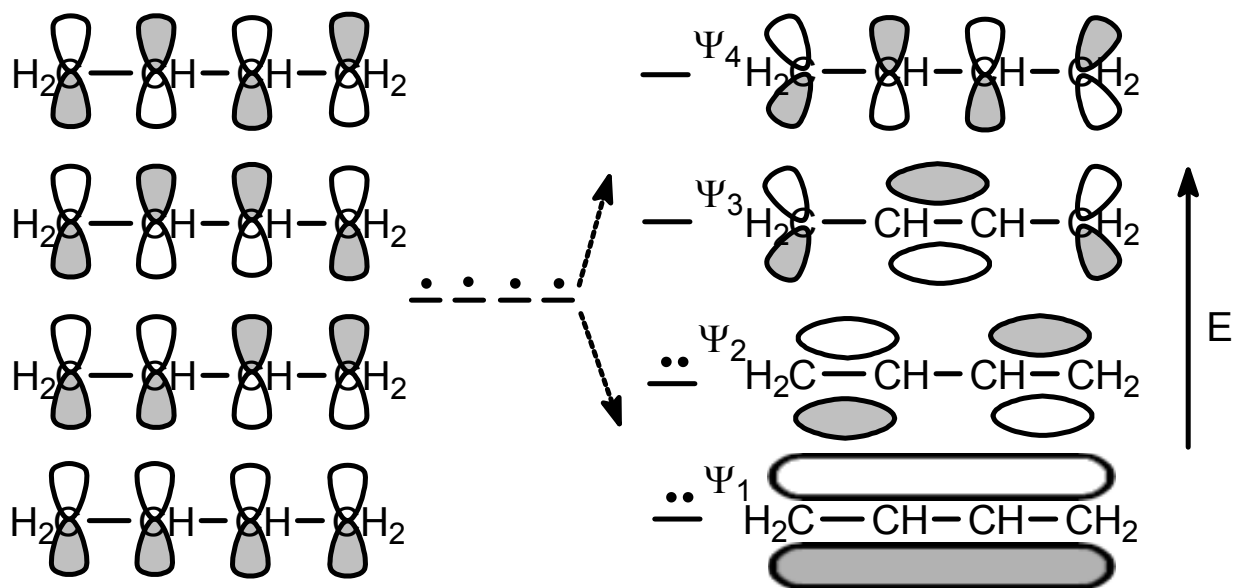
$H_2C = CH_2$

bonding

E

1, 3-Butadiene

At first glance we might think that this would be just like two ethylenes hooked together: a π and π^* orbital between carbons 1 and 2 and also between carbons 3 and 4. However, this overlooks the interaction that is possible between the p orbital on carbon-2 and the one on carbon-3. In fact, the four atomic p orbitals can interact with four different phase arrangements giving four π-type molecular orbitals. This is shown in the figure below. Each of the p atomic orbitals has the same energy and each contains one electron. Each can interact with a neighbor in a bonding way (the orbitals are in phase, , and can overlap), an antibonding way (the orbitals are out of phase, , and cancel each other out between the atoms), or a nonbonding way (the neighboring p orbital makes no contribution to the molecular orbital that will form:). The result of the interaction of the four p orbitals in 1,3-butadiene is the formation of four molecular orbitals, Ψ_1 through Ψ_4. This is shown schematically in the diagram below.

H_2 ⬣—⬣ H—⬣ H—⬣ H_2 $— \Psi_4$ H_2⬣—⬣H—⬣H—⬣H_2

H_2⬣—⬣H—⬣H—⬣H_2 $— \Psi_3$ H_2⬣—CH＝CH—⬣H_2

H_2⬣—⬣H—⬣H—⬣H_2 $\cdot\cdot$ Ψ_2 H_2C＝CH—CH＝CH_2 E

H_2⬣—⬣H—⬣H—⬣H_2 $\cdot\cdot$ Ψ_1 H_2C—CH—CH—CH_2

The orbital of lowest energy is Ψ_1; it is bonding between each of the carbons. The next higher in energy is Ψ_2; it is bonding between C-1 and C-2 and between C-3 and C-4, but antibonding between C-2 and C-3 because the orbital changes phase here. Both of these orbitals are bonding orbitals, overall: they are of lower energy than the isolated atomic p orbitals. [Since electrons in an atomic p orbital are nonbonding, the energy level of the p orbitals is called the nonbonding energy level.] Ψ_3 and Ψ_4 are antibonding orbitals, overall: they are of higher energy than the isolated atomic p orbitals.

The four electrons from the atomic p orbitals go into Ψ_1 and Ψ_2, the two bonding π orbitals, because these are of lowest energy and each, like any orbital, can accommodate two electrons.

Finally, it might be noted that the conjugated 1,3-butadiene system is more stable than an isolated diene because the total energy of the four electrons in Ψ_1 and Ψ_2 turns out to be less than the energy of four electrons in two isolated π bonds.

Benzene

Each carbon "starts" with a p atomic orbital containing one electron. These orbitals are perpendicular to the ring, but parallel to each other. These atomic "basis" orbitals are shown in the figure below. Each p orbital interacts ("overlaps") with two neighbors. This gives rise to six π-type orbitals, Ψ_1 through Ψ_6. Ψ_1 through Ψ_3 are bonding orbitals; Ψ_4 through Ψ_6 are antibonding. It turns out that Ψ_1 is the lowest energy orbital. Ψ_2 and Ψ_3 are *degenerate, i.e.* they have the same energy, and it is higher than the energy of Ψ_1. The electrons in the three occupied bonding orbitals give rise to one doughnut of electron density above the ring and one below, containing a total of 6 π electrons. This aromatic electronic delocalization results in considerable stabilization – more than is observed in the case of conjugated aliphatic compounds.

Benzene Molecular Orbitals

$$\Psi_6 = -\phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6$$

$$\Psi_4 = -\phi_1 + \phi_2 - \phi_3 - \phi_4 + \phi_5 - \phi_6$$

$$\Psi_5 = \phi_1 - \phi_3 + \phi_4 - \phi_6$$

ϕ_6 ϕ_5 ϕ_4

E

↑↑↑↑↑↑

ϕ_1 ϕ_2 ϕ_3

$$\Psi_2 = \phi_1 + \phi_2 + \phi_3 - \phi_4 - \phi_5 - \phi_6$$

$$\Psi_3 = \phi_1 - \phi_3 - \phi_4 + \phi_6$$

$$\Psi_1 = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6$$
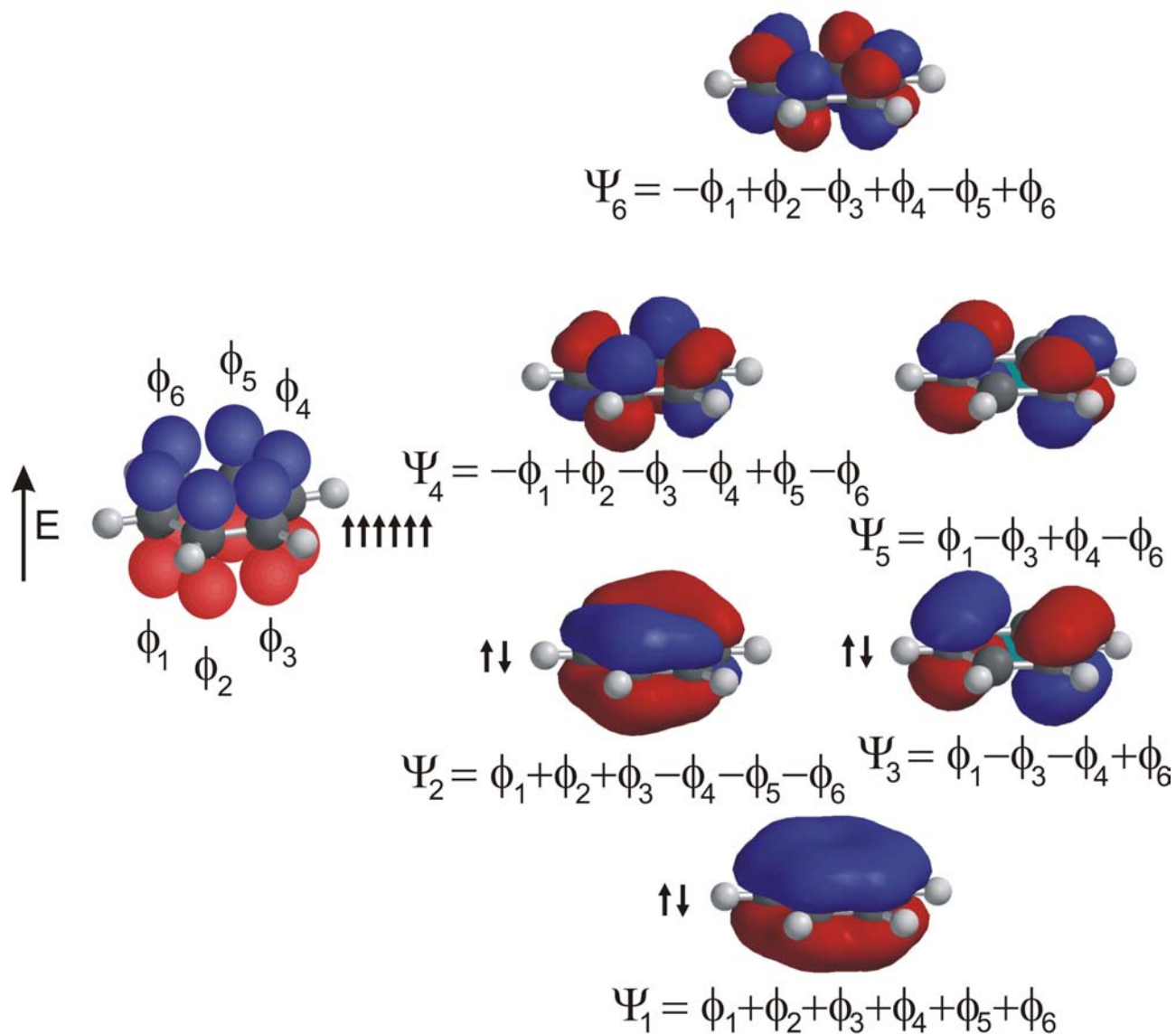
Six atomic 2p orbitals   Six benzene molecular orbitals

9

Because of the π-electrons, benzene, and other aromatic compounds, frequently act as Lewis bases or nucleophiles; thus, they are suscepable to *electrophilic attack*. Because of the stability associated with the delocalized electrons, this feature tends to be retained in the products; consequently, these reactions are usually *substitutions, not additions.*

E^+ + [benzene ring] ⟶ E[benzene ring] + H^+
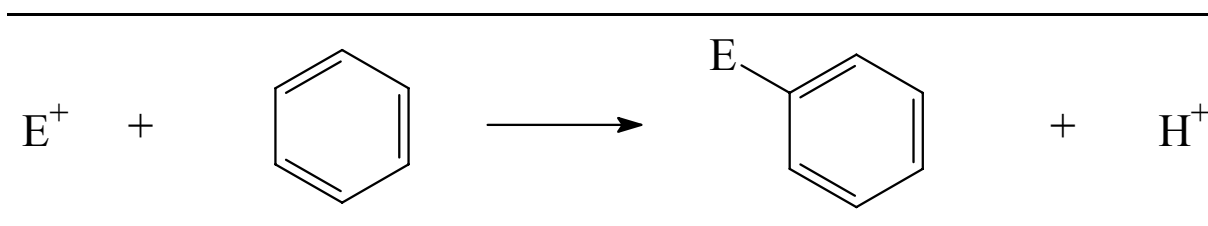
How stable is benzene?

Compared to what?

Compared to isolated π-bonds, and conjugated, non-aromatic π-systems.

Heats of Hydrogenation of Cyclic Unsaturated Molecules

Reactant	Product	ΔH°_{h}	$n \times \Delta H^{\circ}_{h}$ (C_6H_{12})	"Stability"
cyclohexene	cyclohexane	28.6 kcal	28.6 kcal	0 kcal
1,3-cyclo-hexadiene	cyclohexane	55.4	57.2	1.8
benzene	cyclohexane	49.8	85.8	36

Is aromatic stability shared by all monocyclic compounds with conjugated π systems?

 etc.?
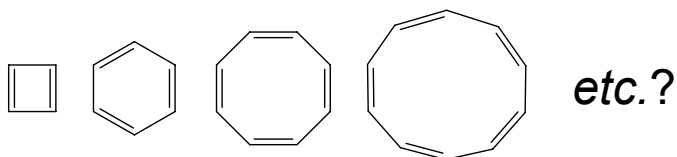
No.
Aromatic stability seems to be associated with

❋   completely filled π bonding orbitals

❋   completely filled or empty π non-bonding orbitals

❋   completely vacant π antibonding orbitals.

Do I need to do Huckel MO calculations to tell what π orbitals exist in one of these molecules and whether or not they are filled?
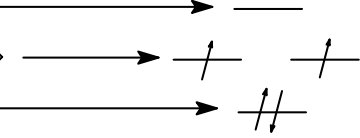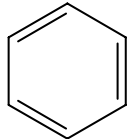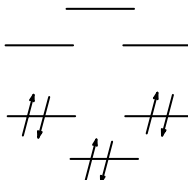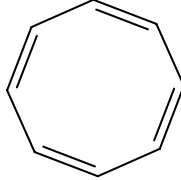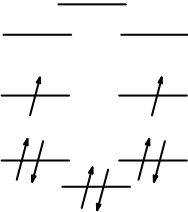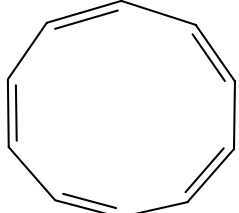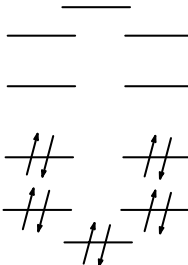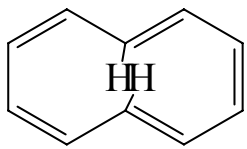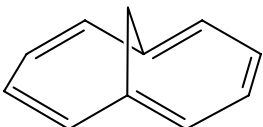
No.

Use the polygon mnemonic to find the orbitals, and fill them with the π electrons in order of increasing energy.

THE POLYGON MNEMONIC

Draw the molecule as a regular polygon and rotate it around its center so one apex is pointing down. Each apex corresponds to a π molecular orbital. The center of the polygon corresponds to the non-bonding energy level (same energy as an isolated p atomic orbital); orbitals of lower energy are bonding; orbitals of higher energy are anti-bonding.

Examples

				Status

— anti-bonding
⫲ ⫲ non-bonding
⫶⫶ bonding

Anti-aromatic

— anti-bonding
— —

⫲ ⫲ bonding
⫶⫶

Aromatic

— anti-bonding
— —
⫲ ⫲ non-bonding
⫶⫶ ⫶⫶ bonding
⫶⫶

**Not aromatic-
non-planar,
ordinary alkene**

— anti-bonding
— —
— —
⫲ ⫲ bonding
⫶⫶ ⫶⫶
⫶⫶

**Not aromatic-
too much angle
strain to be planar**

**Not aromatic-
too much steric
strain to be planar**

Aromatic

13

Is this the simplest way to predict whether or not a monocyclic conjugated polyene is aromatic?

No.

Well...

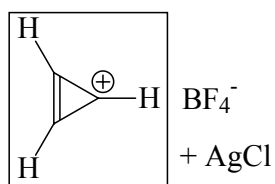If a monocyclic conjugated polyene consisting only of π centers is planar,

☞ it will be aromatic if it contains 4n+2 π electrons, where n is 0, 1, 2 ...

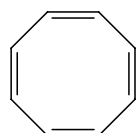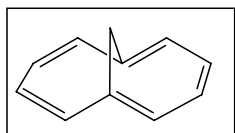☞ it will be anti-aromatic if it contains 4n π electrons.

Some examples ---

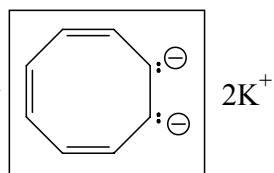4n + 2 π Electrons: Aromatic Moieties

<u>n = 0, 2 π electrons</u> | <u>n = 1, 6 π electrons</u>

H
⊕
—H BF_4^-
H

+ AgCl

AgBF$_4$

H
—H
Cl
H

H
⊖ : K^+
+ HO-t-Bu

H
H
+ K^+ $^-$O-t-Bu
pK_a = 16

H
⊕ HSO_4^-
+ H_2O

H OH
+ dilute H_2SO_4

:N—H
pyrrole

N
:
pyridine

<u>n = 2, 10 π electrons</u>

+ 2 Kº →
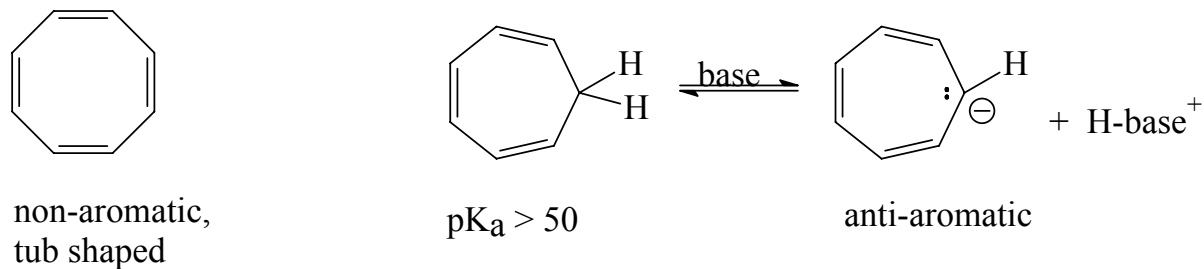
: ⊖
: ⊖ 2K$^+$
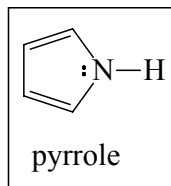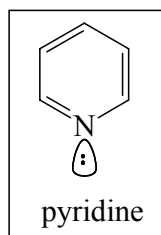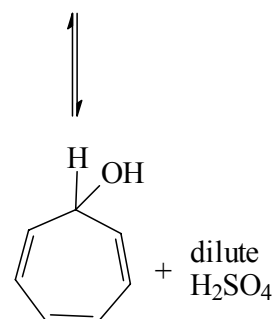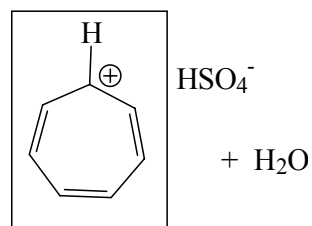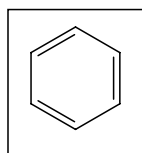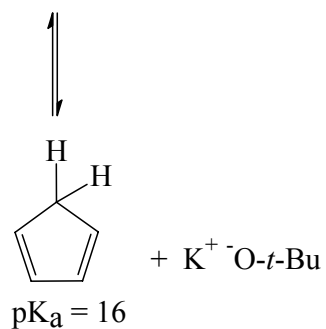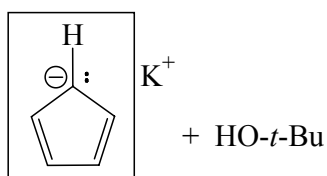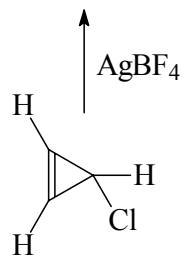
8 π electrons,
tub shaped,
not aromatic

10 π electrons,
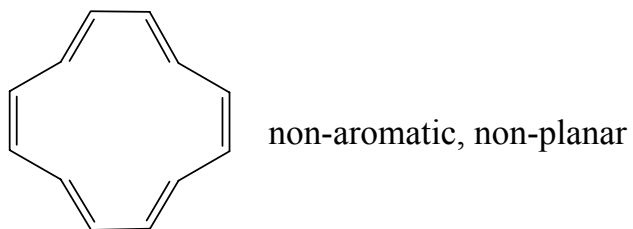planar, aromatic

4n π Electrons: Non- or Anti-Aromatic Moieties

<u>n = 1, 4 π electrons, antiaromatic</u>
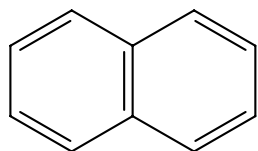

<u>n = 2, 8 π electrons, antiaromatic if planar</u>

non-aromatic,
tub shaped

$pK_a > 50$
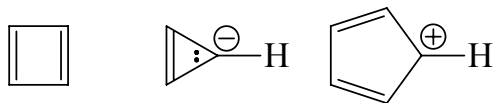
anti-aromatic

<u>n = 3, 12 π electrons, antiaromatic if planar</u>

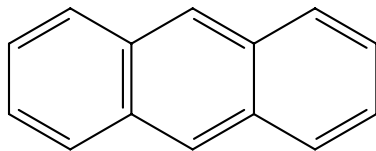non-aromatic, non-planar

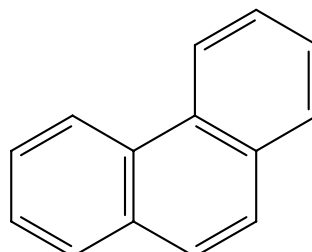*Polycyclic (polynuclear) Aromatic Hydrocarbons*

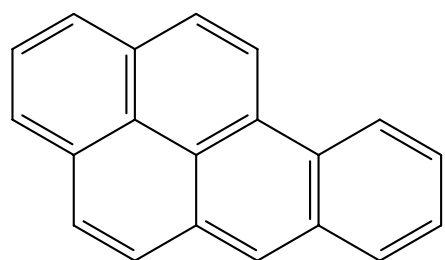Examples ---

naphthalene   anthracene   phenanthrene

benzo[a]pyrene, carcinogenic,
found in cigarette smoke

These compounds are aromatic, but do not have as much
stabilization per ring as benzene. Therefore, although they
undergo electrophilic substitutions, they are more likely than
benzene to undergo some addition reactions, especially if
this results in benzene rings in the products.
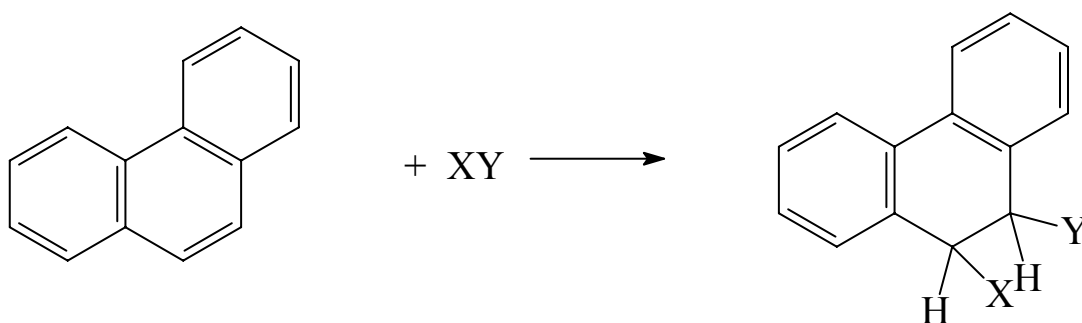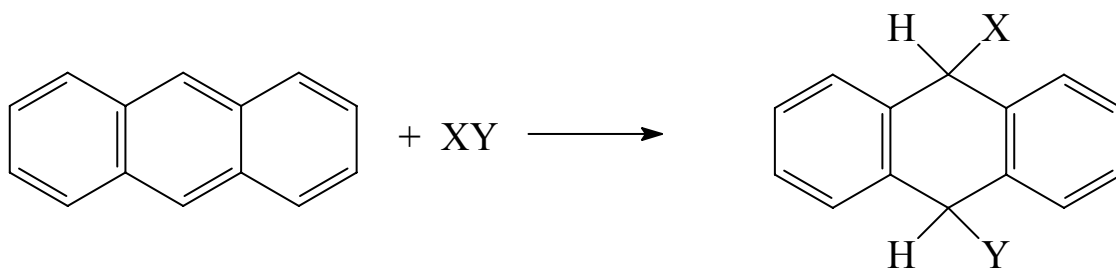
Sources of Aromatic Compounds

Aromatic hydrocarbons may be obtained from ---

1) petroleum – not rich in aromatics, but has some.

2) reforming cycloalkanes from petroleum, *eg*
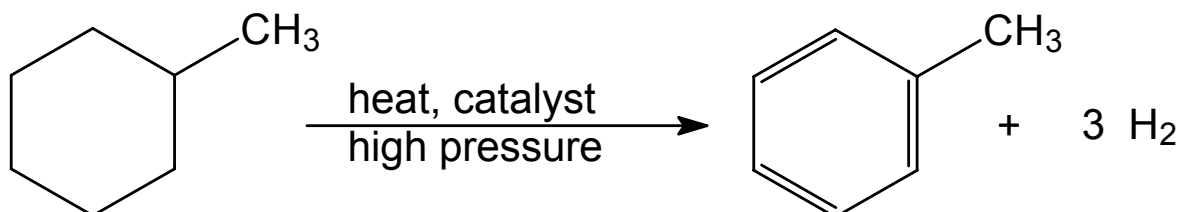
3)   coal tar and coal gas.

Coal derives from plants which have suffered partial decay and been subjected to heat and pressure.

plants ---> peat ---> lignite ---> bituminous (soft) coal ---> ---> anthracite (hard)

Bituminous coal is a good source of aromatic compounds. Destructive distillation of it forms coal gas, coal tar, and coke. Coal tar is rich in aromatic hydrocarbons, bases (*eg,* pyridine), and phenolic (Ar-OH) compounds. [Ar- is shorthand for an aromatic ring, just as R- is shorthand for an alkyl group.]

bituminous coal   heat, no air

non-volatile → coke (blast furnaces, fuel)

volatile → coal gas and coal tar

Rich in aromatic compounds: benzene, toluene, xylenes, *etc.*