Chapter 14

AROMATIC COMPOUNDS

Early History

In the early 19th century, whale oil was an important commercial product. Pyrolysis of the oil produced a gas used to light theaters and public buildings in London. A volatile aromatic (pleasant smelling) liquid separated when the gas was compressed for distribution in tanks. The famous English scientist Michael Faraday, Director of the Royal Institution, investigated this liquid and found that it contained carbon and hydrogen in equal atomic proportions.

This same liquid was later isolated from the tar distilled from coal and was named benzene. Other aromatic compounds were similarly isolated from plant and animal sources during the first half of the 19th century.

A Structural Puzzle

In 1834 the German chemist Eilhardt Mitscherlich produced benzene from benzoic acid:

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + CaO \longrightarrow \underset{\text{Benzene}}{C_6H_6} + CaCO_3$$

His work showed the molecular formula of benzene is C_6H_6.

Aliphatic and Aromatic Hydrocarbons

By the mid-19th century, the Theory of Valence (Kekule, Couper, Butlerov) showed that most known organic compounds had about twice as many hydrogen atoms as carbon atoms. A pattern of atomic linkages was rapidly emerging, except for the "aromatic" compounds.

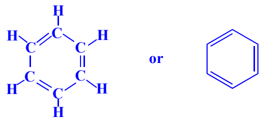
Two broad classes of organic compounds were defined: **aliphatic** ("fatlike") and **aromatic**. The two types differed in their hydrogen/carbon ratios and their chemical reactivities.

The aromatic compounds retained a six-carbon unit during chemical changes, and benzene (C_6H_6) was the parent compound to the other aromatics.

But what structure for benzene was consistent with the Theory of Valence?

The Kekule Structure for Benzene

In 1865 August Kekule proposed a structure for benzene consistent with the new Theory of Valence. The tetravalency of carbon was satisfied by a hexagon with alternating single and double bonds. The low hydrogen to carbon ratio in benzene was now understood.

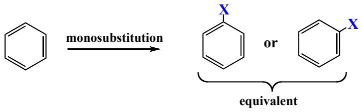


Kekule structure for benzene, C_6H_6

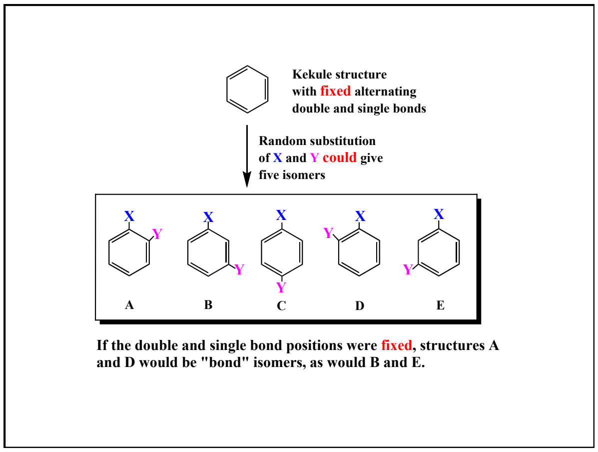
A Problem

Kekule recognized a problem with this structure.

In substitution reactions, benzene yields only a single monosubstitution product, which means that all 6 H's in benzene are equivalent. The Kekule structure predicts this result.



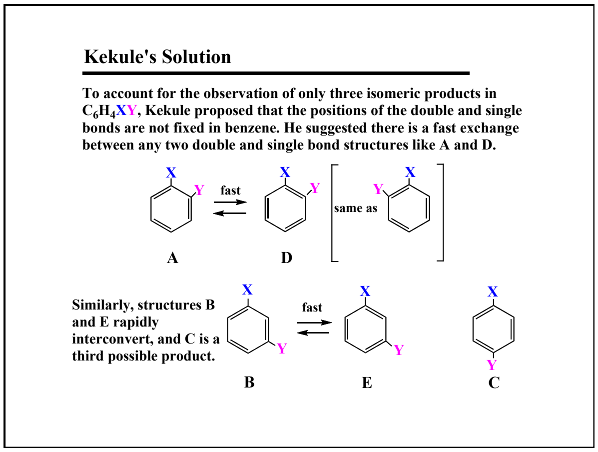
But, for disubstituted benzenes, $C_6H_4X_2$ or C_6H_4XY, the Kekule structure predicts a maximum of 5 different products (isomers), but only 3 different products have ever been obtained.



Kekule structure with fixed alternating double and single bonds

Random substitution of X and Y could give five isomers

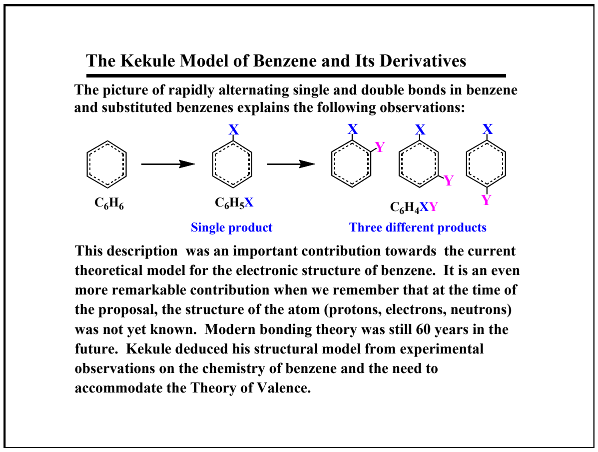
If the double and single bond positions were fixed, structures A and D would be "bond" isomers, as would B and E.



Kekule's Solution

To account for the observation of only three isomeric products in C_6H_4XY, Kekule proposed that the positions of the double and single bonds are not fixed in benzene. He suggested there is a fast exchange between any two double and single bond structures like A and D.

Similarly, structures B and E rapidly interconvert, and C is a third possible product.



The Kekule Model of Benzene and Its Derivatives

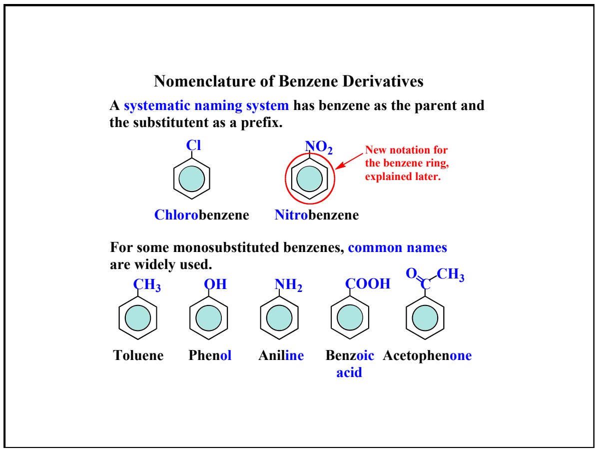
The picture of rapidly alternating single and double bonds in benzene and substituted benzenes explains the following observations:

C_6H_6 → C_6H_5X → C_6H_4XY

Single product

Three different products

This description was an important contribution towards the current theoretical model for the electronic structure of benzene. It is an even more remarkable contribution when we remember that at the time of the proposal, the structure of the atom (protons, electrons, neutrons) was not yet known. Modern bonding theory was still 60 years in the future. Kekule deduced his structural model from experimental observations on the chemistry of benzene and the need to accommodate the Theory of Valence.



Nomenclature of Benzene Derivatives

A systematic naming system has benzene as the parent and the substitutent as a prefix.

New notation for the benzene ring, explained later.

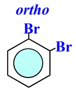
Chlorobenzene Nitrobenzene

For some monosubstituted benzenes, common names are widely used.

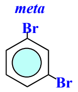
Toluene Phenol Aniline Benzoic acid Acetophenone

Disubstituted Benzenes

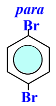
The relative positions of the substituents may be indicated by either of two systems. In one, the prefixes *ortho* (*o*), *meta* (*m*) and *para* (*p*) indicate the following relative positions:



o-Dibromobenzene

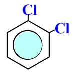


m-Dibromobenzene

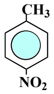


p-Dibromobenzene

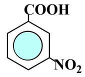
In the second system, the relative positions may be indicated by numbers. When a common name is used for a monosubstituted benzene, that original substituent is understood to be at position 1.



1,2-Dichlorobenzene
(*o*-Dichlorobenzene)



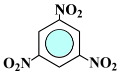
4-Nitrotoluene
(*p*-Nitrotoluene)



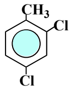
3-Nitrobenzoic acid
(*m*-Nitrobenzoic acid)

Benzenes with Three or More Substituents

These compounds must be named using numbers to indicate the relative positions of the substituents around the ring. When a common name is used for a parent monosubstituted benzene, that original substituent is understood to be at position 1. The *o,m,p* naming system is never used when there are three or more substituents.



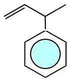
1,3,5-Trinitrobenzene



2,4-Dichlorotoluene

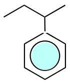
The Phenyl and Benzyl Substituent Groups

The C_6H_5 group in a structure sometimes is named as a phenyl substituent.



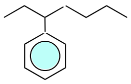
3-Phenyl-1-butene

Focus is on unsaturated side chain, even if short



1-Methylpropylbenzene

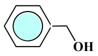
Focus is on unsaturated ring when side chain has fewer carbons



3-Phenylheptane

Focus is on side chain when it has more carbons than the ring

Be careful to recognize that BENZYL is not another name for the C_6H_5 phenyl group but for the $C_6H_5CH_2$ phenylmethyl group.

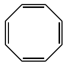


Benzyl alcohol or
phenylmethanol

Demise of the Kekule Model

During the late 19th and early 20th century, it was thought that the unique chemical properties of benzene (discussed below) were due to the alternating double and single bonds in the cyclic structure.

In 1911 Richard Willstätter dismissed this idea by synthesizing cyclooctatetraene and showing that it possessed the chemical reactivity of an alkene. It did not display the "aromatic" chemical properties of benzene.

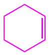


Cyclooctatetraene
(not "aromatic")

The Special Nature of Benzene

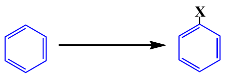
Benzene does not show the chemical reactivity of an alkene. The aromatic ring structure shows unusual stability. It is of markedly lower reactivity, and when it does react it is typically by substitution rather than addition.

Comparative Chemical Reactivity of Cyclohexene and Benzene

Reagents		
Cold, dilute $KMnO_4$	rapid hydroxylation	no reaction
Br_2/CCl_4	rapid addition	no reaction
HI	rapid addition	no reaction
H_2/Ni	hydrogenation 25 °C, 20 psi	very slow hydrogenation >100 °C, 1500 psi

Aromatic Substitution Reactions

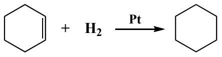
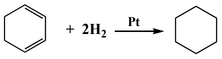
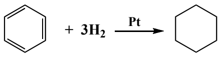
The chemical reactivity of benzene is characterized by substitution, which preserves the aromatic ring, rather than by addition.



This pattern of reactivity suggests the aromatic ring is unusually stable.

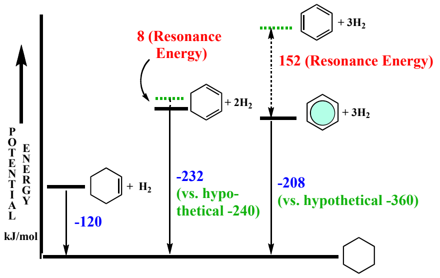
RESONANCE ENERGY: A Quantitative Measure of Stability

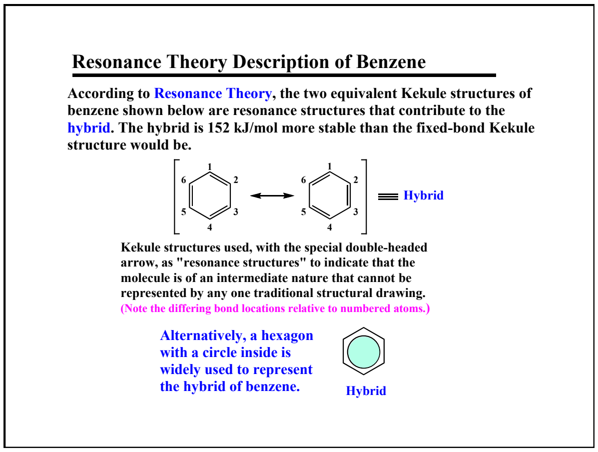
The heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene are compared below. The expected values for $\Delta H^o_{H_2}$ are based on the observed $\Delta H^o_{H_2}$ for cyclohexene. The lower heat release observed with the conjugated systems (resonance energy) measures their special stabilization.

Heats of Hydrogenation	$\Delta H^o_{H_2}$ (kJ/mol) Observed	Expected	Resonance Energy (kJ/mol)
	-120	-----	-----
	-232	-240	8
	-208	-360	152

RESONANCE ENERGY: Energy Diagram Depiction

The special stabilization of benzene (152 kJ/mol) revealed by comparing the observed heat of hydrogenation of benzene (-208 kJ/mol) with the hypothetical value for 1,3,5-cyclohexatriene (-360 kJ/mol) is called its resonance energy. This comparison, and that for 1,3-cyclohexadiene, are shown in the potential energy diagram below.



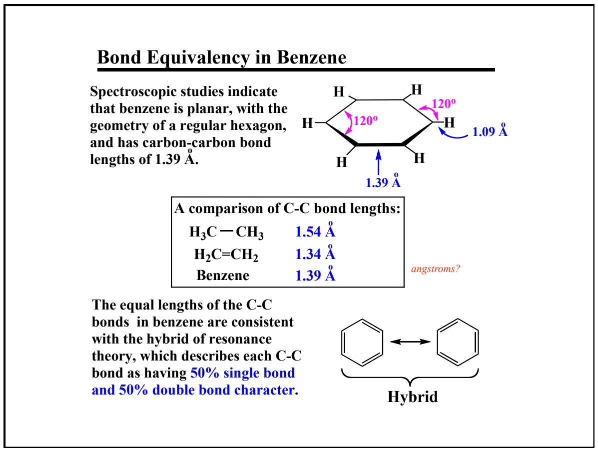


Resonance Theory Description of Benzene

According to **Resonance Theory**, the two equivalent Kekule structures of benzene shown below are resonance structures that contribute to the **hybrid**. The hybrid is 152 kJ/mol more stable than the fixed-bond Kekule structure would be.

Kekule structures used, with the special double-headed arrow, as "resonance structures" to indicate that the molecule is of an intermediate nature that cannot be represented by any one traditional structural drawing.
(Note the differing bond locations relative to numbered atoms.)

Alternatively, a hexagon with a circle inside is widely used to represent the hybrid of benzene.



Bond Equivalency in Benzene

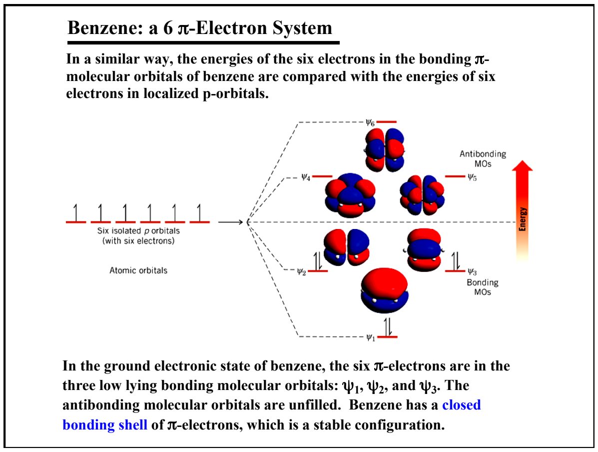
Spectroscopic studies indicate that benzene is planar, with the geometry of a regular hexagon, and has carbon-carbon bond lengths of 1.39 Å.

A comparison of C-C bond lengths:

H_3C-CH_3	1.54 Å
$H_2C{=}CH_2$	1.34 Å
Benzene	1.39 Å

angstroms?

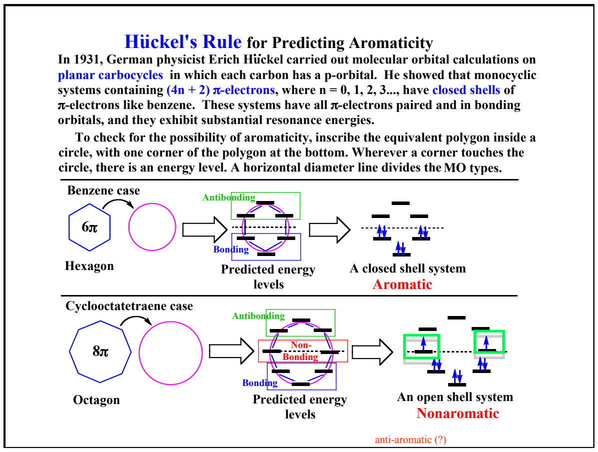
The equal lengths of the C-C bonds in benzene are consistent with the hybrid of resonance theory, which describes each C-C bond as having **50% single bond and 50% double bond character**.



Benzene: a 6 π-Electron System

In a similar way, the energies of the six electrons in the bonding π-molecular orbitals of benzene are compared with the energies of six electrons in localized p-orbitals.

In the ground electronic state of benzene, the six π-electrons are in the three low lying bonding molecular orbitals: ψ_1, ψ_2, and ψ_3. The antibonding molecular orbitals are unfilled. Benzene has a **closed bonding shell** of π-electrons, which is a stable configuration.



Hückel's Rule for Predicting Aromaticity

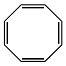
In 1931, German physicist Erich Hückel carried out molecular orbital calculations on **planar carbocycles** in which each carbon has a p-orbital. He showed that monocyclic systems containing **(4n + 2) π-electrons**, where n = 0, 1, 2, 3..., have **closed shells** of π-electrons like benzene. These systems have all π-electrons paired and in bonding orbitals, and they exhibit substantial resonance energies.

To check for the possibility of aromaticity, inscribe the equivalent polygon inside a circle, with one corner of the polygon at the bottom. Wherever a corner touches the circle, there is an energy level. A horizontal diameter line divides the MO types.

anti-aromatic (?)

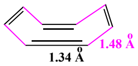
not closed system?

Properties of Cyclooctatetraene



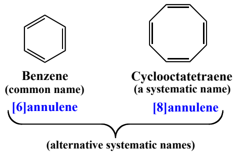
As predicted by the Huckel rule, this compund is nonaromatic and has the chemical properties of an alkene. It is a yellow liquid, bp 152 ºC, that is stable at low temperatures but polymerizes upon heating. It is slowly oxidized by air and easily undergoes catalytic hydrogenation.

Being non-aromatic there is no stabilizing resonance energy to be gained from having all p-orbitals parallel, and the molecule is tub shaped. Also, its non-aromaticity means that it has localized single and double bonds, as indicated by their bond lengths:



The Annulenes

Annulenes are monocyclic compounds with alternating double and single bonds. The ring size is indicated by a number inside square brackets before the word "annulene."

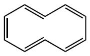


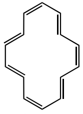
Prediction of Aromaticity of the Annulenes

The Hückel (4n + 2) π electron rule predicts whether or not an annulene is expected to show aromatic properties. Even if an annulene has (4n + 2) π electrons, $\boxed{\text{it will not be aromatic if it cannot be planar.}}$

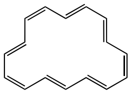
Over the past 40 years, many annulenes have been synthesized and studied.

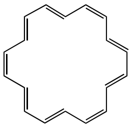
Predictions of Aromaticity by the Hückel Rule





	[10]annulene	[14]annulene
Prediction	Yes	Yes
Observation	No (not planar)	Yes





	[16]annulene	[18]annulene
Prediction	No (not 4n + 2)	Yes
Observation	No	Yes

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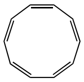
[10]annulene

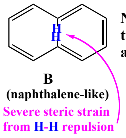
The Trouble with [10]Annulene

[10]Annulene does not show the properties and stability of an aromatic compound despite the prediction by the Hückel rule.

The required planar structures (with extensive overlap of the p-orbitals) in both the all-*cis* (A) and naphthalene-like (B) forms are unstable because of strain energy so both are non-aromatic.

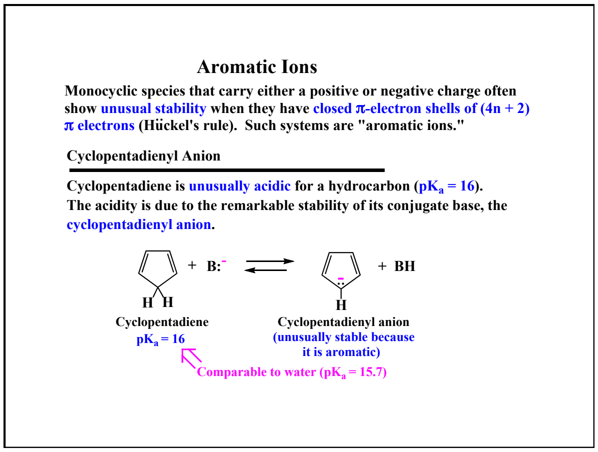


A
(all *cis*)
Severe angle strain



B
(naphthalene-like)
Severe steric strain from H-H repulsion

Note that here two double bonds are *trans*.



Aromatic Ions

Monocyclic species that carry either a positive or negative charge often show **unusual stability** when they have **closed π-electron shells of (4n + 2) π electrons** (Hückel's rule). Such systems are "aromatic ions."

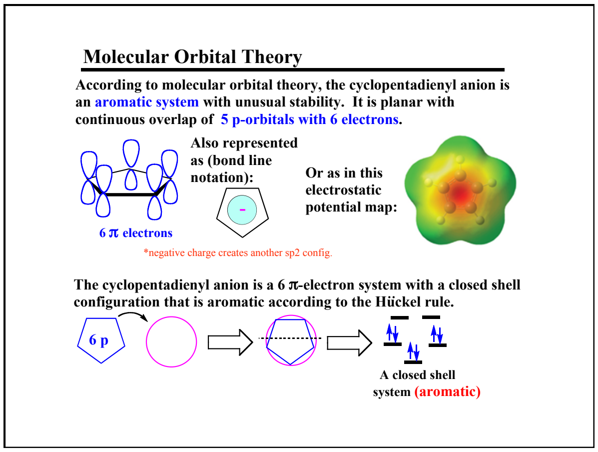
Cyclopentadienyl Anion

Cyclopentadiene is **unusually acidic** for a hydrocarbon ($pK_a = 16$). The acidity is due to the remarkable stability of its conjugate base, the **cyclopentadienyl anion**.

Cyclopentadiene
$pK_a = 16$

Cyclopentadienyl anion
(unusually stable because it is aromatic)

Comparable to water ($pK_a = 15.7$)



Molecular Orbital Theory

According to molecular orbital theory, the cyclopentadienyl anion is an **aromatic system** with unusual stability. It is planar with continuous overlap of **5 p-orbitals with 6 electrons**.

6 π electrons

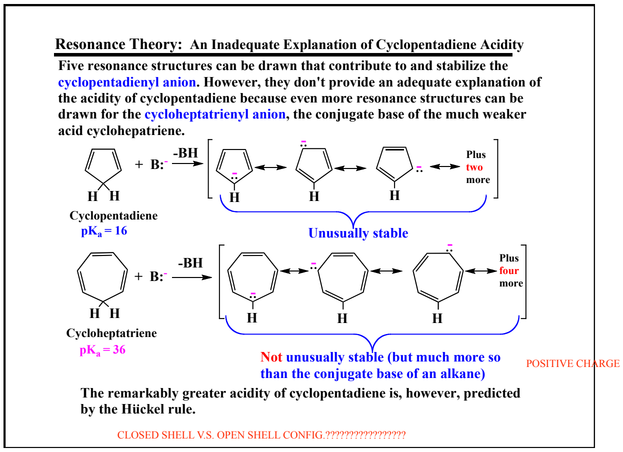
Also represented as (bond line notation):

Or as in this electrostatic potential map:

*negative charge creates another sp2 config.

The cyclopentadienyl anion is a 6 π-electron system with a closed shell configuration that is aromatic according to the Hückel rule.

A closed shell system (aromatic)



Resonance Theory: An Inadequate Explanation of Cyclopentadiene Acidity

Five resonance structures can be drawn that contribute to and stabilize the **cyclopentadienyl anion**. However, they don't provide an adequate explanation of the acidity of cyclopentadiene because even more resonance structures can be drawn for the **cycloheptatrienyl anion**, the conjugate base of the much weaker acid cyclohepatriene.

Cyclopentadiene
$pK_a = 16$

Unusually stable

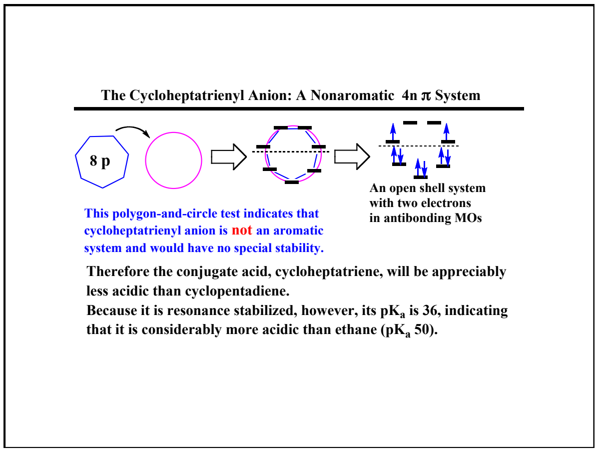
Cycloheptatriene
$pK_a = 36$

Not unusually stable (but much more so than the conjugate base of an alkane)

POSITIVE CHARGE

The remarkably greater acidity of cyclopentadiene is, however, predicted by the Hückel rule.

CLOSED SHELL V.S. OPEN SHELL CONFIG.?????????????????

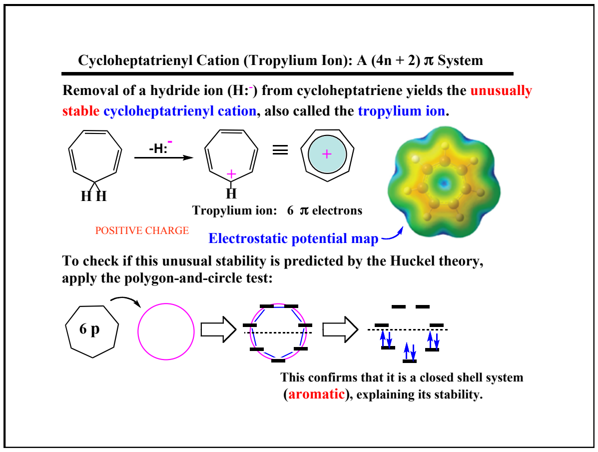


The Cycloheptatrienyl Anion: A Nonaromatic 4n π System

An open shell system with two electrons in antibonding MOs

This polygon-and-circle test indicates that cycloheptatrienyl anion is **not** an aromatic system and would have no special stability.

Therefore the conjugate acid, cycloheptatriene, will be appreciably less acidic than cyclopentadiene.
Because it is resonance stabilized, however, its pK_a is 36, indicating that it is considerably more acidic than ethane (pK_a 50).



Cycloheptatrienyl Cation (Tropylium Ion): A (4n + 2) π System

Removal of a hydride ion (H:$^-$) from cycloheptatriene yields the unusually stable cycloheptatrienyl cation, also called the tropylium ion.

Tropylium ion: 6 π electrons

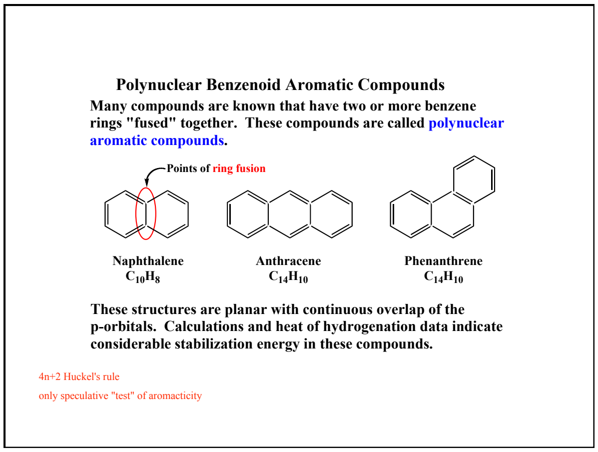
POSITIVE CHARGE

Electrostatic potential map

To check if this unusual stability is predicted by the Huckel theory, apply the polygon-and-circle test:

This confirms that it is a closed shell system (aromatic), explaining its stability.

same molecule -
anionic = non
aromatic
cationic = aromatic



Polynuclear Benzenoid Aromatic Compounds

Many compounds are known that have two or more benzene rings "fused" together. These compounds are called polynuclear aromatic compounds.

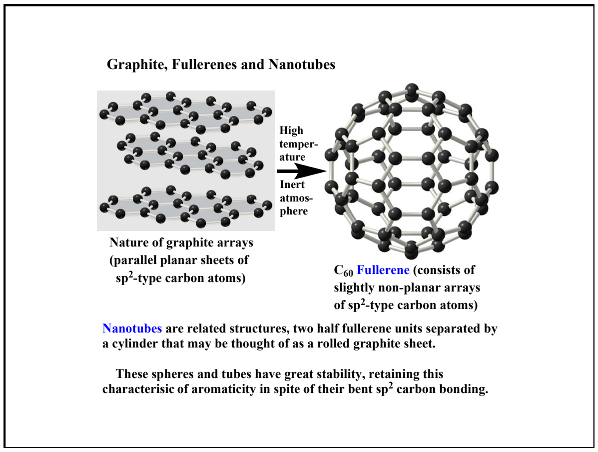
Naphthalene $C_{10}H_8$

Anthracene $C_{14}H_{10}$

Phenanthrene $C_{14}H_{10}$

These structures are planar with continuous overlap of the p-orbitals. Calculations and heat of hydrogenation data indicate considerable stabilization energy in these compounds.

4n+2 Huckel's rule
only speculative "test" of aromacticity



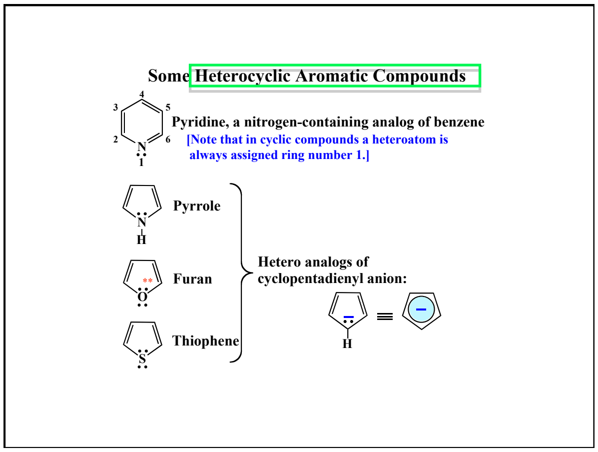
Graphite, Fullerenes and Nanotubes

Nature of graphite arrays (parallel planar sheets of sp^2-type carbon atoms)

C_{60} Fullerene (consists of slightly non-planar arrays of sp^2-type carbon atoms)

Nanotubes are related structures, two half fullerene units separated by a cylinder that may be thought of as a rolled graphite sheet.

These spheres and tubes have great stability, retaining this characterisic of aromaticity in spite of their bent sp^2 carbon bonding.



Some Heterocyclic Aromatic Compounds

Pyridine, a nitrogen-containing analog of benzene
[Note that in cyclic compounds a heteroatom is always assigned ring number 1.]

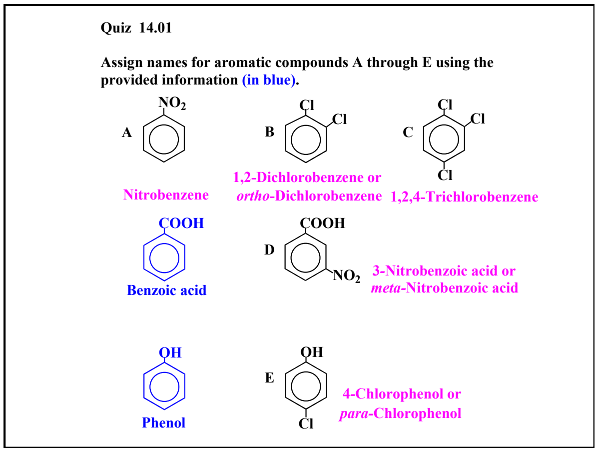
Pyrrole

Furan

Thiophene

Hetero analogs of cyclopentadienyl anion:

**that lone pair delocalizes across pentagon creating stability and O sp2 orbital(???)



Quiz 14.01

Assign names for aromatic compounds A through E using the provided information (in blue).

A: **Nitrobenzene**

B: **1,2-Dichlorobenzene or *ortho*-Dichlorobenzene**

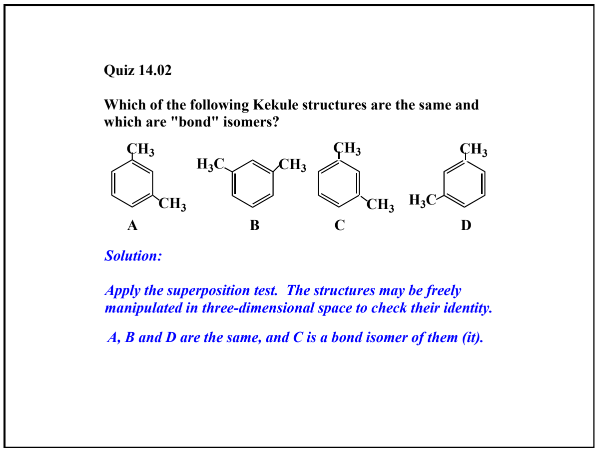
C: **1,2,4-Trichlorobenzene**

Benzoic acid

D: **3-Nitrobenzoic acid or *meta*-Nitrobenzoic acid**

Phenol

E: **4-Chlorophenol or *para*-Chlorophenol**



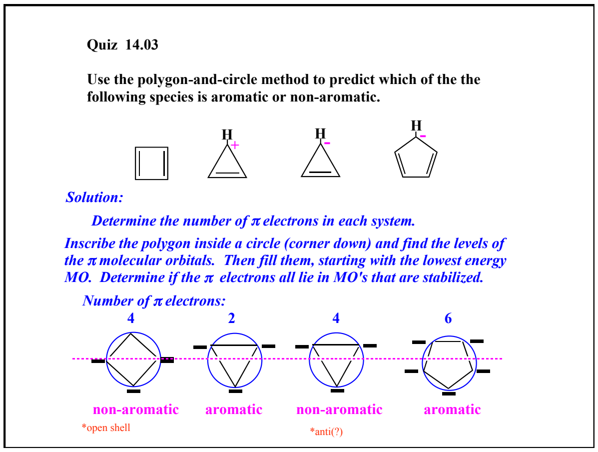
Quiz 14.02

Which of the following Kekule structures are the same and which are "bond" isomers?

Solution:

Apply the superposition test. The structures may be freely manipulated in three-dimensional space to check their identity.

A, B and D are the same, and C is a bond isomer of them (it).



Quiz 14.03

Use the polygon-and-circle method to predict which of the the following species is aromatic or non-aromatic.

Solution:

Determine the number of π electrons in each system.

Inscribe the polygon inside a circle (corner down) and find the levels of the π molecular orbitals. Then fill them, starting with the lowest energy MO. Determine if the π electrons all lie in MO's that are stabilized.

Number of π electrons:

non-aromatic *open shell

aromatic

non-aromatic *anti(?)

aromatic