

A Structural Puzzle

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



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.

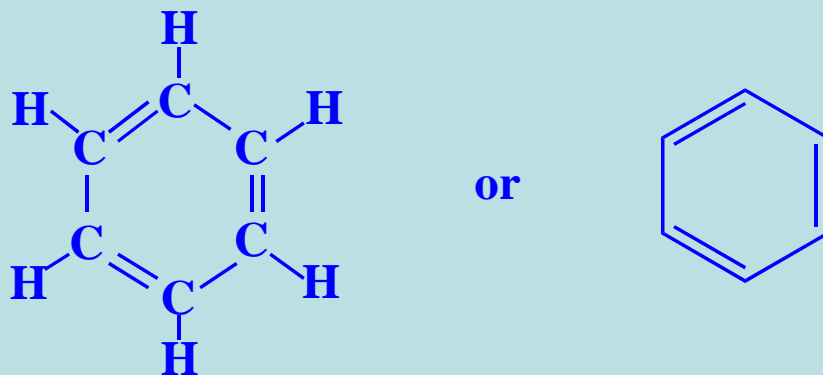
Two broad classes of organic compounds were defined: **aliphatic** ("fatlike") and **aromatic**. The two types differed in their hydrogen/carbon ratios and their chemical reactivities.

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.

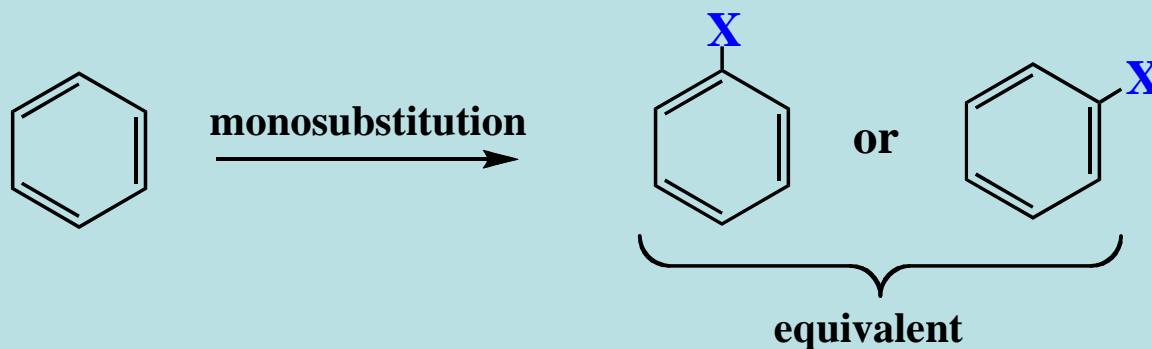


Kekule structure for benzene, C_6H_6

A Problem

Kekule recognized a problem with this structure.

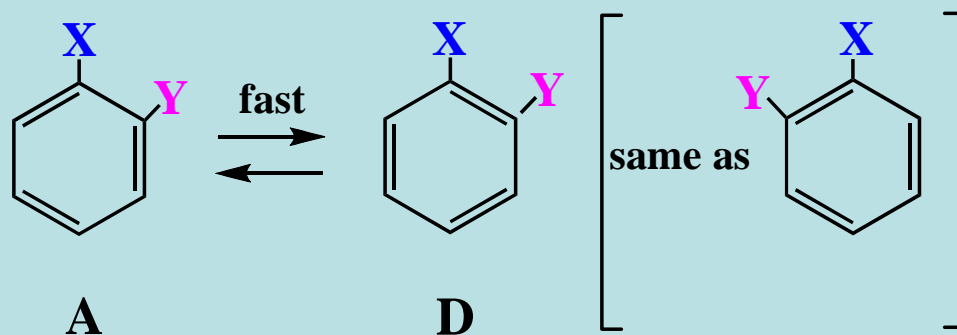
In substitution reactions, benzene yields only a single monosubstitution product, which means that all 6 H's in benzene are equivalent. The Kekule structure predicts this result.



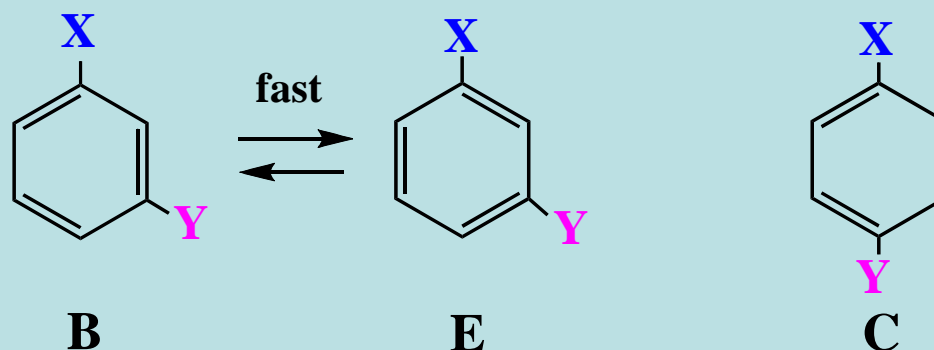
But, for disubstituted benzenes, $C_6H_4X_2$ or C_6H_4XY , the Kekule structure predicts a maximum of **5 different products** (isomers), but only **3 different products** have ever been obtained.

Kekule'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.

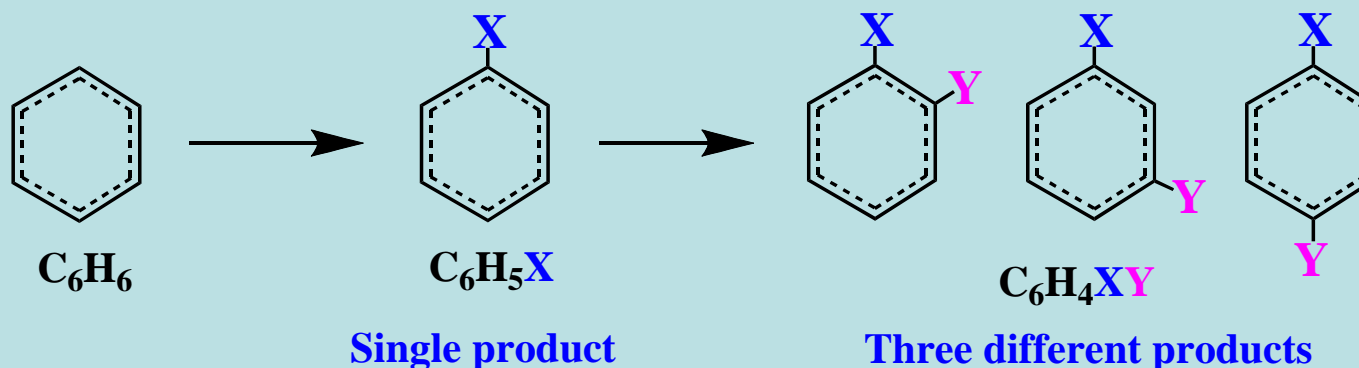


Similarly, structures B and E rapidly interconvert, and C is a third possible product.



The Kekule Model of Benzene and Its Derivatives

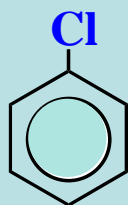
The picture of rapidly alternating single and double bonds in benzene and substituted benzenes explains the following observations:



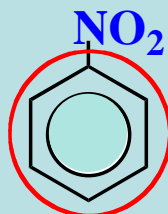
This description was an important contribution towards the current theoretical model for the electronic structure of benzene. It is an even more remarkable contribution when we remember that at the time of the proposal, the structure of the atom (protons, electrons, neutrons) was not yet known. Modern 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 substituent as a prefix.



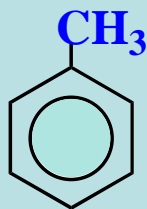
Chlorobenzene



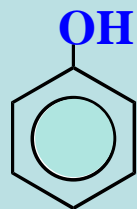
Nitrobenzene

New notation for the benzene ring, explained later.

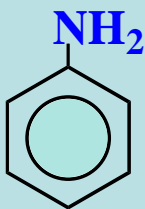
For some monosubstituted benzenes, **common names** are widely used.



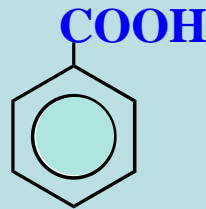
Toluene



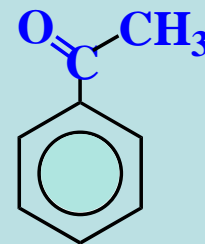
Phenol



Aniline



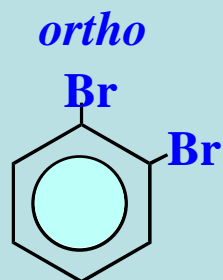
Benzoic acid



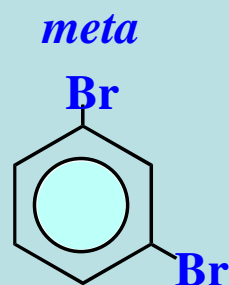
Acetophenone

Disubstituted Benzenes

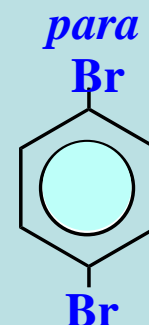
The relative positions of the substituents may be indicated by either of two systems. In one, the prefixes *ortho* (*o*), *meta* (*m*) and *para* (*p*) indicate the following relative positions:



o-Dibromobenzene

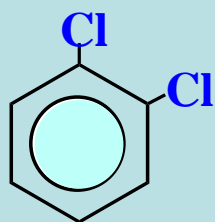


m-Dibromobenzene

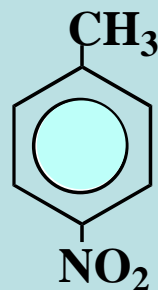


p-Dibromobenzene

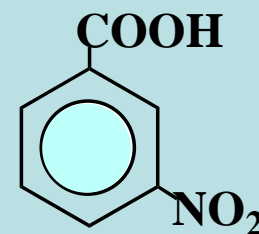
In the second system, the relative positions may be indicated by **numbers**. When a common name is used for a monosubstituted benzene, that original substituent is understood to be at position **1**.



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



4-Nitrotoluene
(*p*-Nitrotoluene)



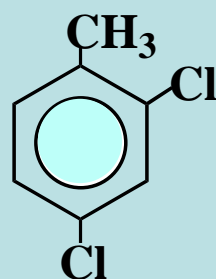
3-Nitrobenzoic acid
(*m*-Nitrobenzoic acid)

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.



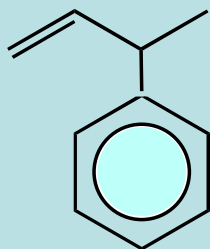
1,3,5-Trinitrobenzene



2,4-Dichlorotoluene

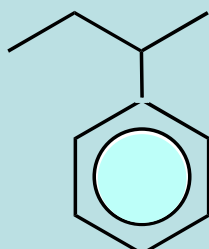
The Phenyl and Benzyl Substituent Groups

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



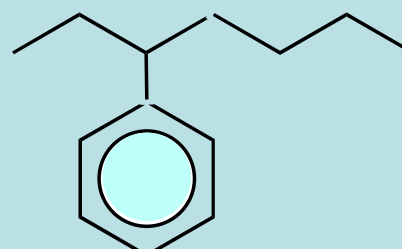
3-Phenyl-1-butene

Focus is on
unsaturated side
chain, even if short



1-Methylpropylbenzene

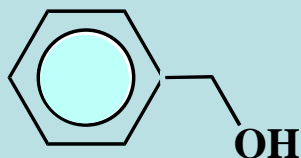
Focus is on unsaturated
ring when side chain has
fewer carbons



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.

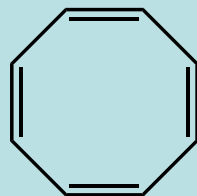


Benzyl alcohol or
phenylmethanol

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.



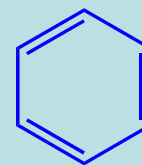
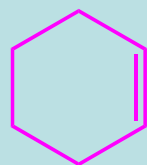
Cyclooctatetraene
(not "aromatic")

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

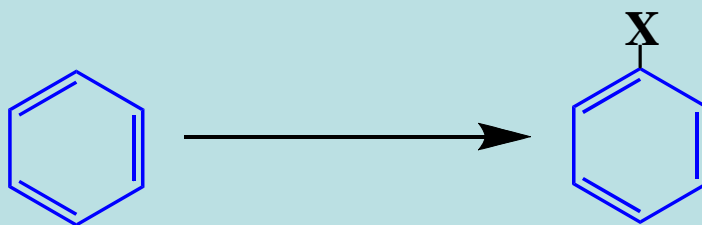
H_2/Ni

hydrogenation
 $25\text{ }^\circ\text{C}$, 20 psi

very slow
hydrogenation
 $>100\text{ }^\circ\text{C}$, 1500 psi

Aromatic Substitution Reactions

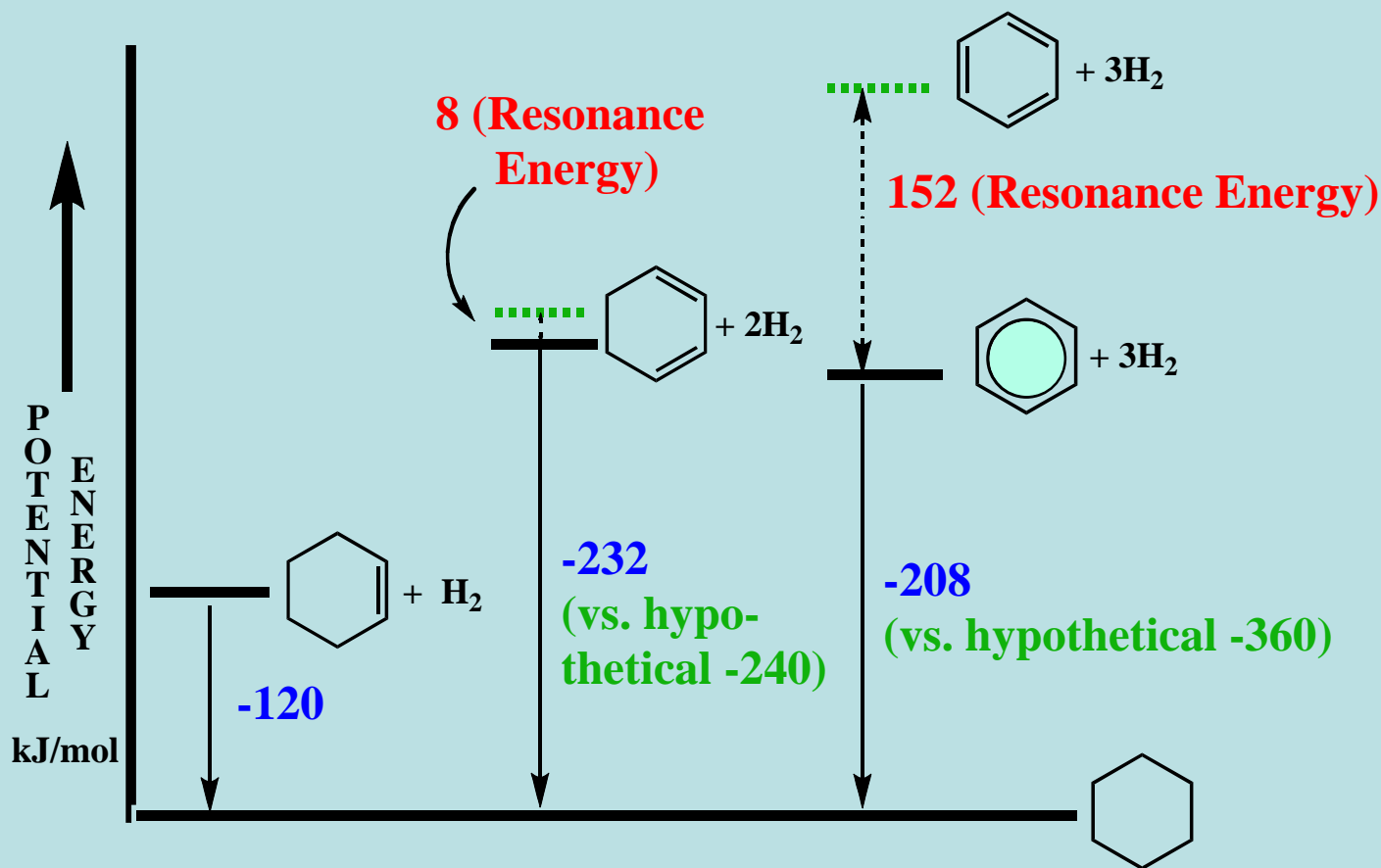
The chemical reactivity of benzene is characterized by **substitution**, which preserves the **aromatic ring**, rather than by **addition**.



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

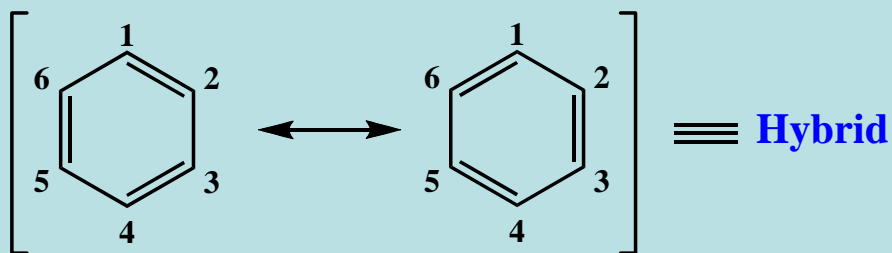
RESONANCE ENERGY: Energy Diagram Depiction

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

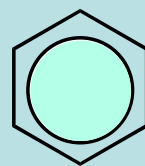
According to **Resonance Theory**, the two equivalent Kekule structures of benzene shown below are resonance structures that contribute to the **hybrid**. The hybrid is 152 kJ/mol more stable than the fixed-bond Kekule structure would be.



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.)

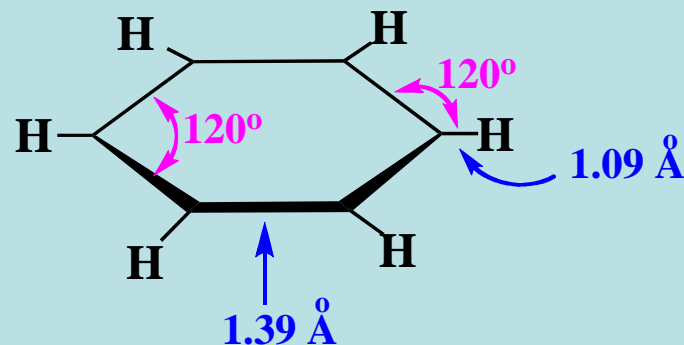
Alternatively, a hexagon with a circle inside is widely used to represent the hybrid of benzene.



Hybrid

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.



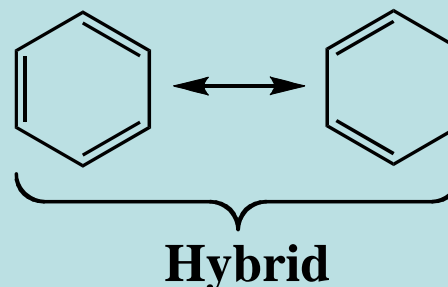
A comparison of C-C bond lengths:

$\text{H}_3\text{C} - \text{CH}_3$ 1.54 Å

$\text{H}_2\text{C} = \text{CH}_2$ 1.34 Å

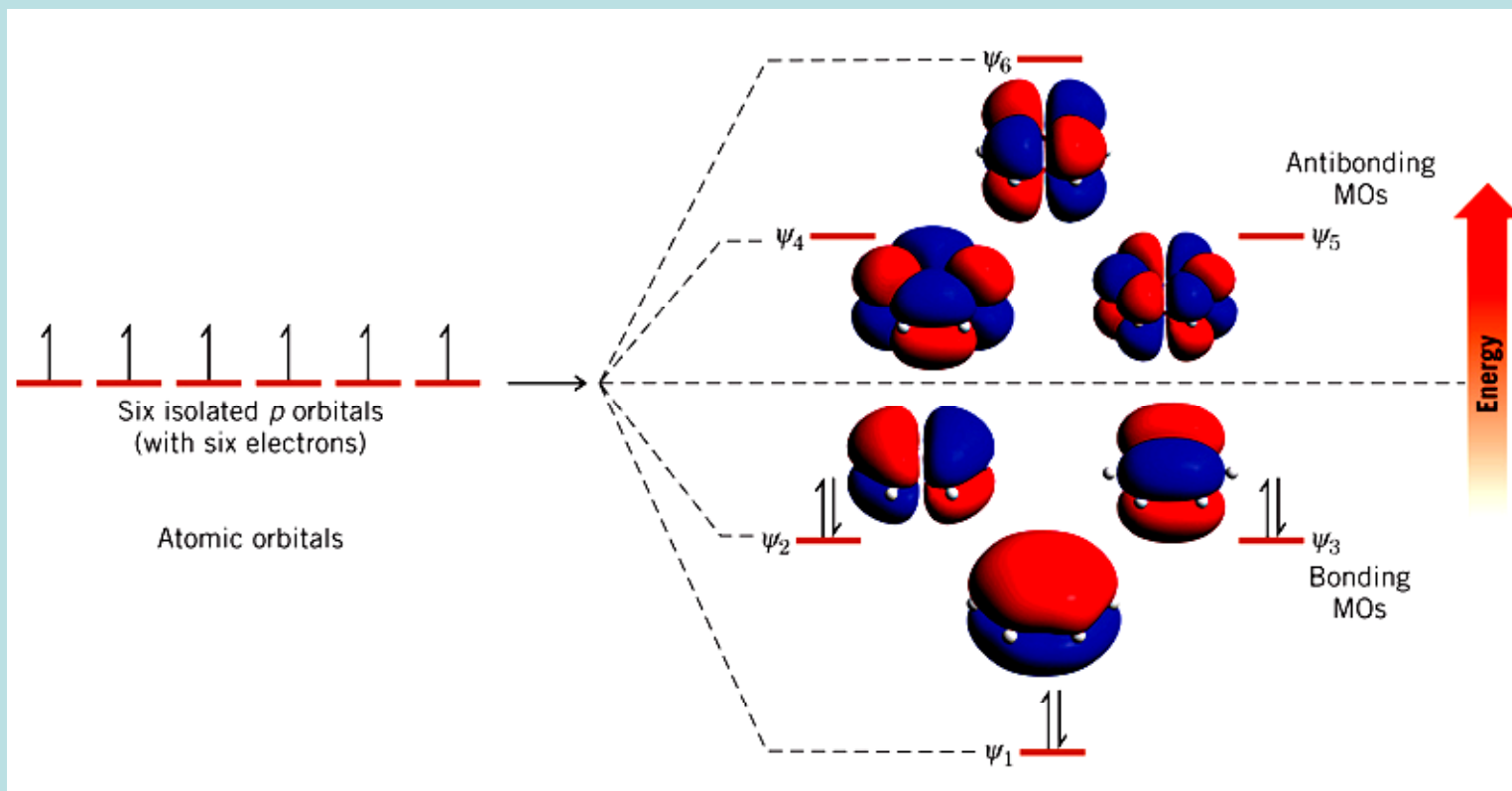
Benzene 1.39 Å

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

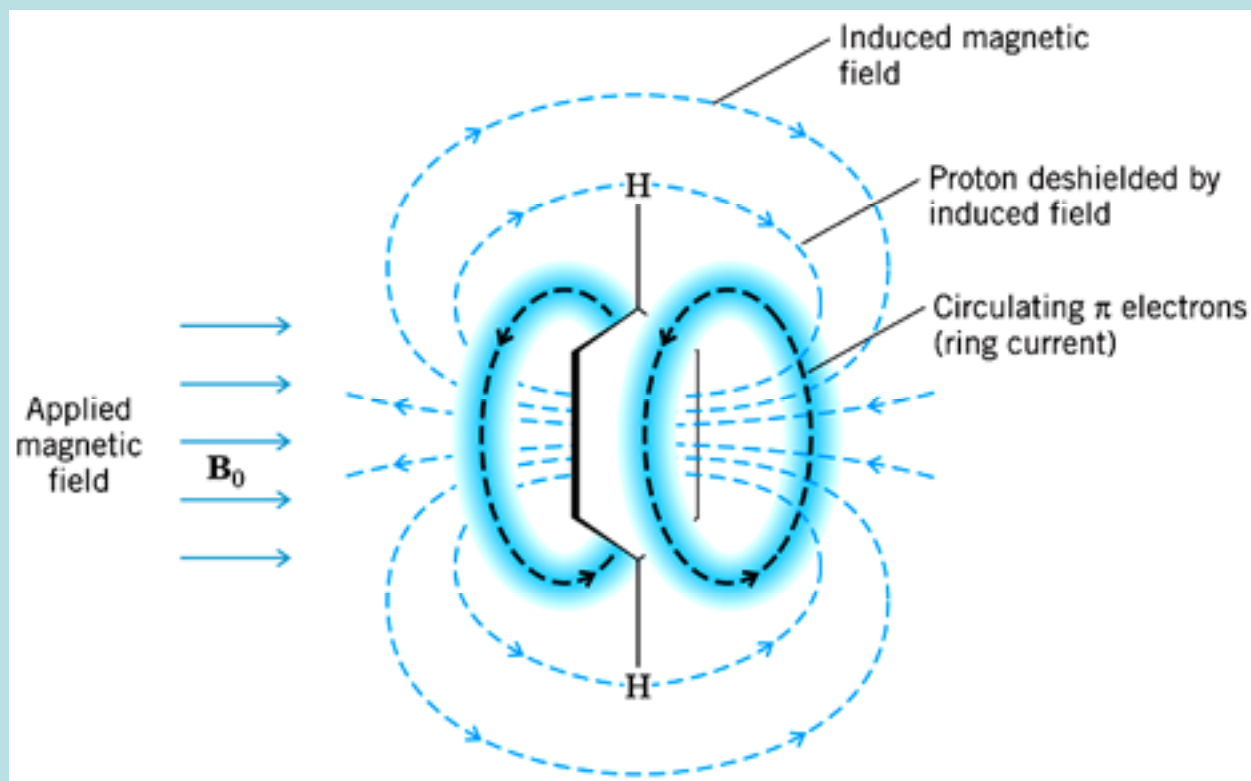
In a similar way, the energies of the six electrons in the bonding π -molecular orbitals of benzene are compared with the energies of six electrons in localized p-orbitals.



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.

Proton NMR Evidence for Electron Delocalization in Benzene and Other Aromatic Compounds

The single unsplit NMR signal at 7.27δ confirms that all hydrogens in benzene are equivalent. The unusually low field δ value is caused by the strong, opposing induced field that is possible because the π electrons are delocalized, permitting a strong ring current.



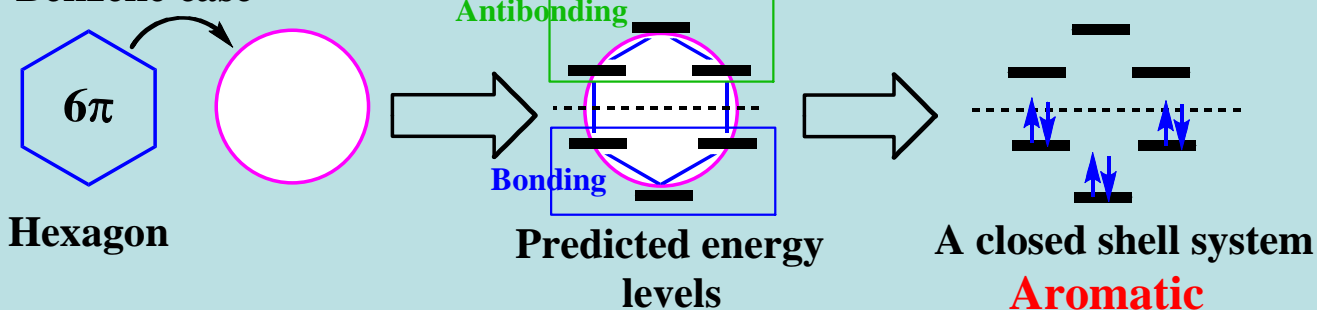
The hydrogens of substituted benzenes absorb in the downfield region of 6.0 to 9.5δ , the exact location and number of peaks depending on the effect of the substituents on electron density.

Hückel's Rule for Predicting Aromaticity

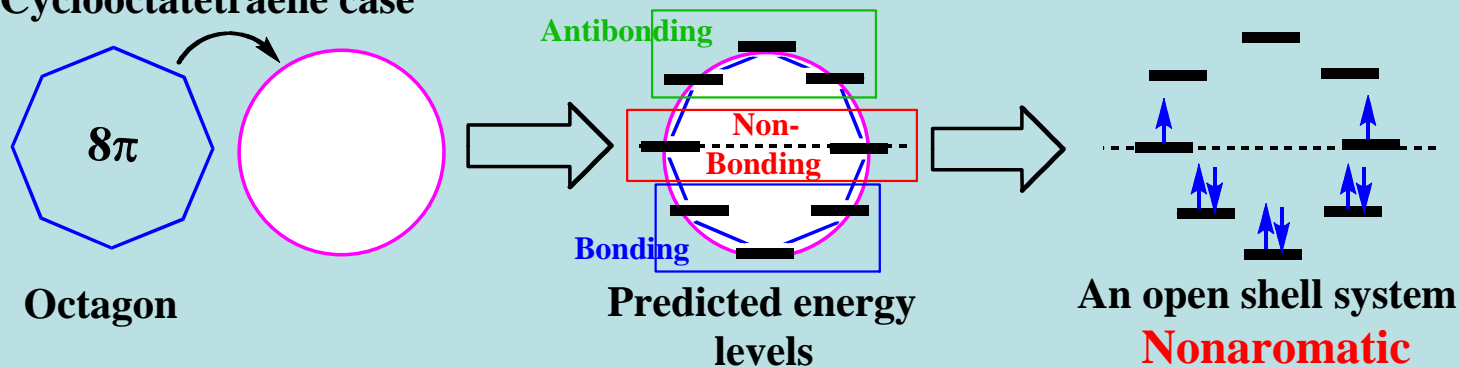
In 1931, German physicist Erich Hückel carried out molecular orbital calculations on **planar carbocycles** in which each carbon has a p-orbital. He showed that monocyclic systems containing $(4n + 2) \pi$ -electrons, where $n = 0, 1, 2, 3, \dots$, have **closed shells** of π -electrons like benzene. 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.

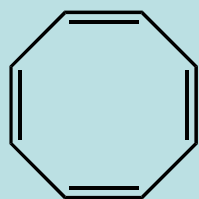
Benzene case



Cyclooctatetraene case

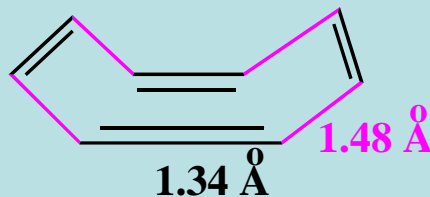


Properties of Cyclooctatetraene



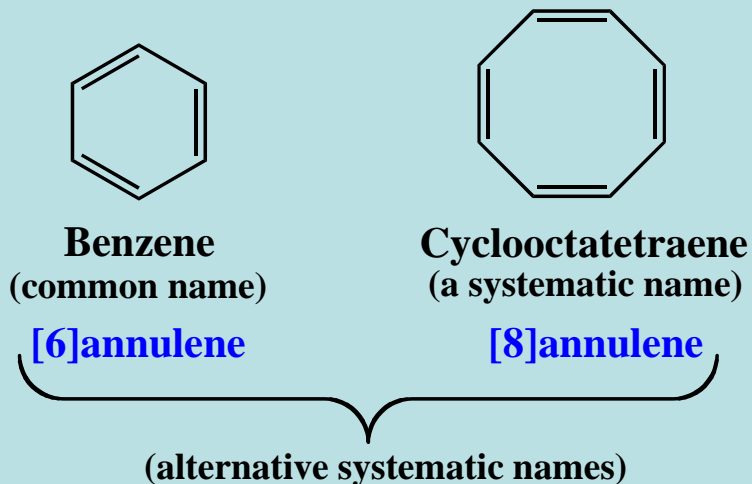
As predicted by the Huckel rule, this compound is nonaromatic and has the chemical properties of an alkene. It is a yellow liquid, bp 152 °C, that is stable at low temperatures but polymerizes upon heating. It is slowly oxidized by air and easily undergoes catalytic hydrogenation.

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."

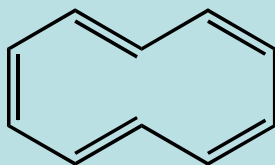


Prediction of Aromaticity of the Annulenes

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, 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



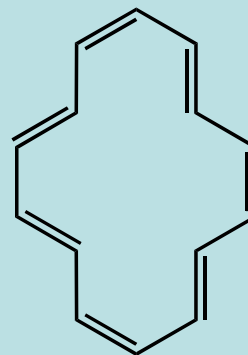
[10]annulene

Yes

Prediction

Observation

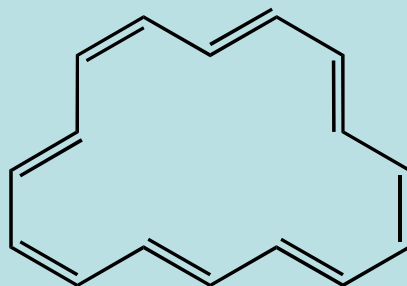
No (not planar)



[14]annulene

Yes

Yes



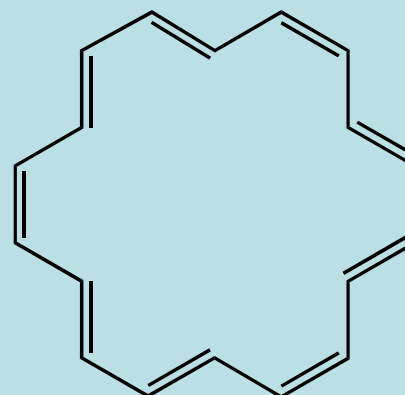
[16]annulene

No (not $4n + 2$)

Prediction

Observation

No



[18]annulene

Yes

Yes

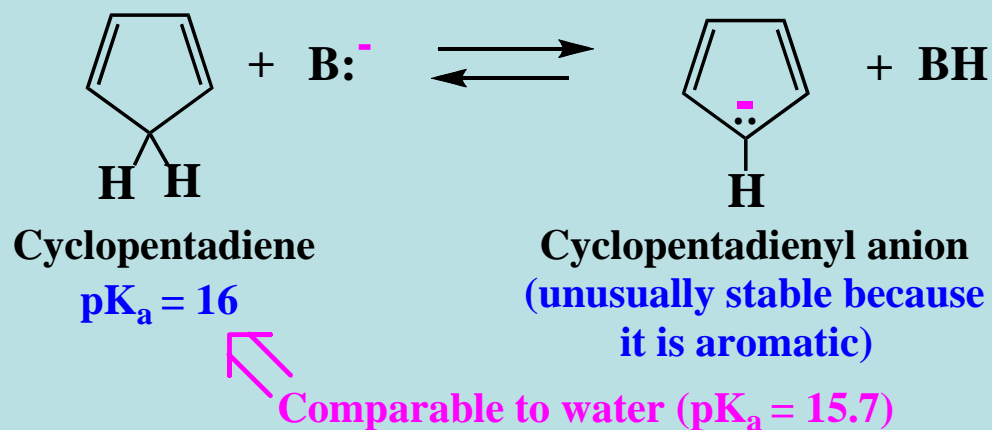
Aromatic Ions

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

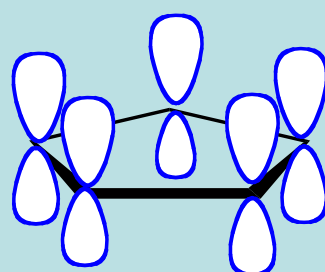
Cyclopentadiene is **unusually acidic** for a hydrocarbon ($\text{pK}_a = 16$).

The acidity is due to the remarkable stability of its conjugate base, the **cyclopentadienyl anion**.



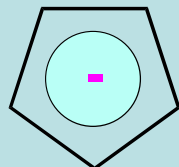
Molecular Orbital Theory

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**.

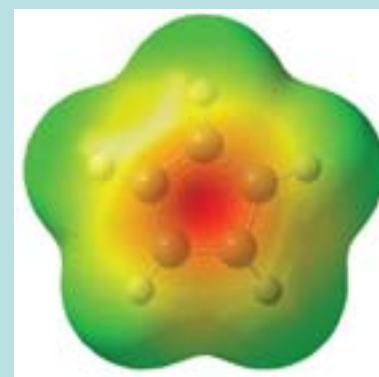


6 π electrons

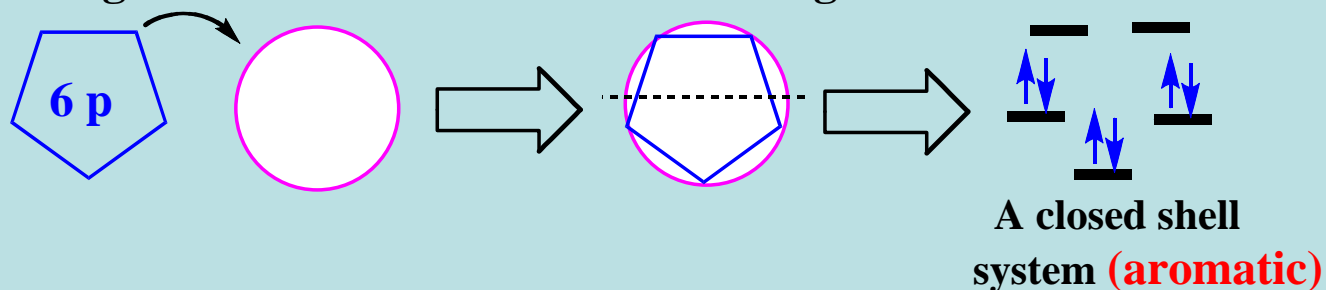
Also represented
as (bond line
notation):



Or as in this
electrostatic
potential map:

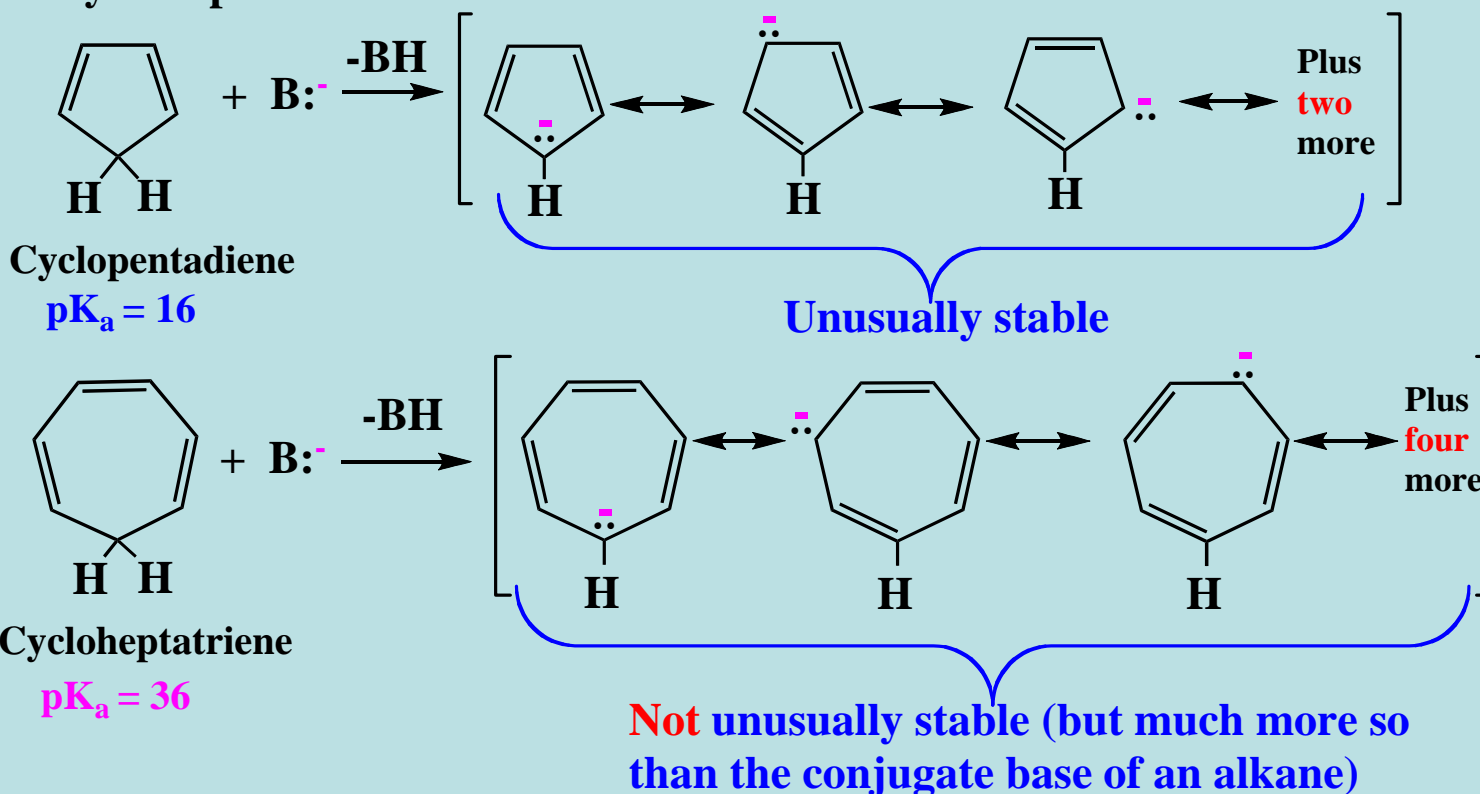


The cyclopentadienyl anion is a 6 π -electron system with a closed shell configuration that is aromatic according to the Hückel rule.



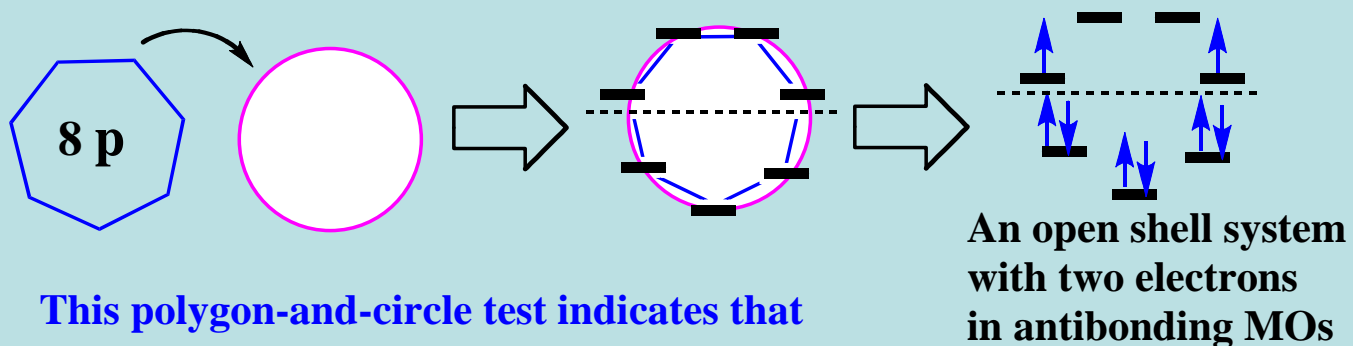
Resonance Theory: An Inadequate Explanation of Cyclopentadiene Acidity

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 cycloheptatriene.



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

The Cycloheptatrienyl Anion: A Nonaromatic $4n \pi$ System



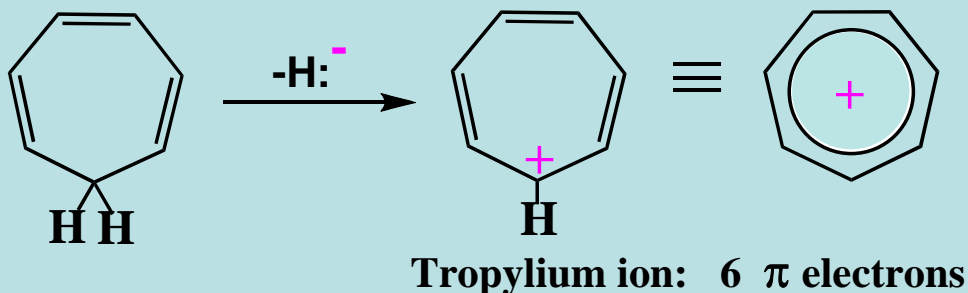
This polygon-and-circle test indicates that cycloheptatrienyl anion is **not** an aromatic system and would have no special stability.

Therefore the conjugate acid, cycloheptatriene, will be appreciably less acidic than cyclopentadiene.

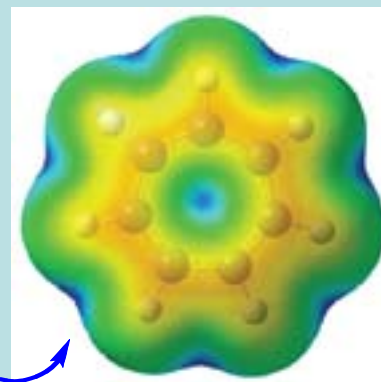
Because it is resonance stabilized, however, its pK_a is 36, indicating that it is considerably more acidic than ethane (pK_a 50).

Cycloheptatrienyl Cation (Tropylium Ion): A $(4n + 2) \pi$ System

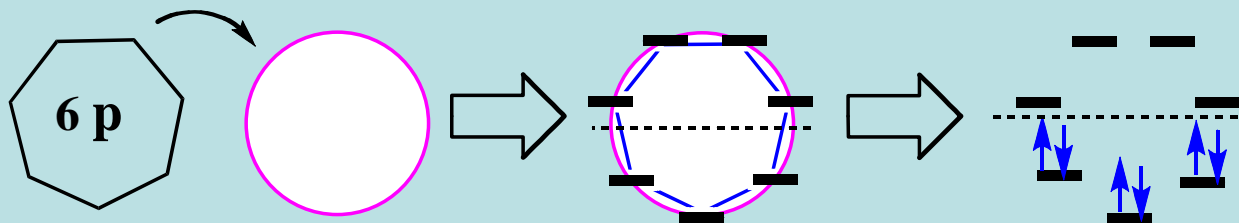
Removal of a hydride ion (H^-) from cycloheptatriene yields the **unusually stable cycloheptatrienyl cation**, also called the **tropylium ion**.



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.