In the systematic nomenclature, benzenes share priority with the alkenes
carboxylic acids > esters > amides > nitriles > aldehydes > ketones > alcohols > thiols > amines > alkenes (benzenes) > alkynes

Systematic nomenclature of benzenes
• If the highest priority group is the benzene ring, the name ends in ...benzene
• Number the ring carbons such that the lowest number is given to a substituent at the first point of difference
• If the benzene ring is treated as a substituent, it is called phenyl

Write the systematic name

“trinitrotoluene (TNT)”

“A polychlorinated biphenyl (PCB)”

Write the systematic name

“tert-butylhydroxyanisole (BHA)”

fed to Penicillium mold to produce penicillin V
Write the systematic name

\[
\text{Cl} \quad \text{Br} \\
\text{Br} \quad \text{Cl}
\]

Many structures for benzene have been proposed

Kekulé 1859
Ladenburg 1870s
Dewar 1870s

Kekulé's structure of benzene was suggested by a dream

"Two snakes seized each other by the tail... their forms whisked mockingly before my eyes."

The structure of benzene is an average of its two Kekulé structures

\[
\begin{align*}
\text{Kekulé structures} & \quad \leftrightarrow \\
\text{Armit-Robinson structure} & \quad \text{or}
\end{align*}
\]

carbon–carbon single bond 1.54 Å
carbon–carbon bonds in benzene 1.40 Å
carbon–carbon double bond 1.33 Å

The six bonding π electrons of benzene occupy the three bonding π MOs

The three nonbonding π MOs of benzene are empty
Benzene enjoys a special stabilization called aromaticity

\[ \Delta H^\circ \text{ of a C}_{sp2}-H \text{ group} = 9 \text{ kcal/mol} \]
\[ \Delta H^\circ \text{ of benzene} = 20 \text{ kcal/mol} \]

Stabilization = \((6 \times 9) - 20 = 34 \text{ kcal/mol}\)

Molecular orbital theory of aromaticity: The Hückel 4N + 2 Rule

To be aromatic, a molecule must have a planar, cyclic array of \(p\) or \(\pi\) orbitals housing two times an odd number of \(\pi\) electrons (2, 6, 10, ..., 4\(N\) + 2, where \(N\) is an integer)

Are these compounds aromatic?

Aromaticity isn't about odor, but some benzene derivatives do smell good

Experimental evidence for aromaticity: diamagnetic (de)shielding in the NMR

Experimental evidence for aromaticity: diamagnetic (de)shielding in the NMR

vanillin
Vanilla mexicana

thymol
Thymus vulgaris
Assign the $^1$H-NMR signals of benzenol (common names: phenol, carboxylic acid)

$\delta$ (ppm)

Aromatic $\pi$ systems: Carbocations that are stable at 25 °C

1H-NMR $\delta$ 11.1, s

Aromatic $\pi$ systems other than benzene: The cyclopentadienide anion

pK$_a$ = 16

stable to 300 °C

1H-NMR $\delta$ 5.5, s

Aromatic $\pi$ systems other than benzene: The tropylium cation

doesn't react with H$_2$O at pH 3

1H-NMR $\delta$ 9.2, s

Aromatic $\pi$ systems: The cyclooctatetraenide dianion

stable in solution

all carbon–carbon bonds 1.4 Å

1H-NMR $\delta$ 5.7, s

Aromatic $\pi$ systems: The cyclononatetraenide anion

mono trans

1H-NMR $\delta$ 7.3–6.4, 8H, m

δ -3.5, 1H, m

all cis

1H-NMR $\delta$ 7, s
Why aren’t these 10 \( \pi \) systems aromatic?

This molecule is planar, but is it aromatic?

Circle the more basic carbonyl oxygen

The product is aromatic; what is its structure?

Cyclobutadiene is destabilized by antiaromaticity

The Hückel 4N Rule

\[ \Delta H^\circ_{\text{r}} \text{ of a } \text{C}_6\text{sp}^2-\text{H group} = 9 \text{ kcal/mol} \]
\[ \Delta H^\circ_{\text{r}} \text{ of cyclobutadiene} = 121 \text{ kcal/mol} \]
\[ E_{\text{strain}} \text{ of cyclobutadiene} = 31 \text{ kcal/mol} \]

Destabilization apart from strain =

\[ 121 - 31 - (4 \times 9) = 54 \text{ kcal/mol} \]

To be antiaromatic, a molecule must have a planar, cyclic array of p or \( \pi \) orbitals housing two times an even number of \( \pi \) electrons (4, 8, 12, ..., 4N, where N is an integer)
Cyclobutadiene is very reactive: it defied efforts at synthesis for 100 years.

**Problem**

Sketch the π MOs of cyclobutadiene; rank them in order of energy.

**Antiaromatic 4 π systems**

8 π electron cyclooctatetraene avoids being antiaromatic by puckering into a "tub".

\[ \Delta H_f^\circ \text{ of a C}_{sp2}-\text{H group} = 9 \text{ kcal/mol} \]
\[ \Delta H_f^\circ \text{ of cyclooctatetraene} = 72 \text{ kcal/mol} \]
Stabilization = \( (8 \times 9) - 72 = 0 \) kcal/mol

**Large-ring antiaromatic systems: Paramagnetic (de)shielding**

Experimental evidence for antiaromaticity: paramagnetic (de)shielding in the NMR.
MO energies of (anti)aromatic compounds follow a regular pattern:

2,6,10,\ldots \pi \text{ systems have a closed shell: aromatic}

4,8,12,\ldots \pi \text{ systems have unpaired electrons in high-energy orbitals: antiaromatic}

Aromatic and antiaromatic rings may contain heteroatoms:

\begin{align*}
\text{pyridine} & \quad E_{\text{stabilization}} = 23 \text{ kcal/mol} \\
\text{furan} & \quad E_{\text{stabilization}} = 16 \text{ kcal/mol} \\
\text{indole} & \\
\end{align*}

Why is pyridine more stabilized than furan?

Are these molecules aromatic, antiaromatic or nonaromatic?

Fused-ring aromatic 10 \pi systems:

\begin{align*}
\text{naphthalene} & \quad E_{\text{stabilization}} = 53 \text{ kcal/mol} \\
\text{azulene} & \quad E_{\text{stabilization}} = 24 \text{ kcal/mol} \\
\end{align*}

Fused-ring antiaromatic 8 \pi systems:

\begin{align*}
\text{Pentalene} & \quad \text{never isolated} \\
\text{stable for 2 hr at 25 \text{ °C in argon atmosphere} } \\
\end{align*}

Incomplete combustion of organics affords fused-ring aromatics:

\begin{align*}
\text{tobacco or gasoline or hot dogs} & \quad \text{O}_2 \\
& \quad 2\text{e}^\ominus \\
& \quad 2\text{H}^\oplus \\
& \quad \text{cytochrome P450} \\
& \quad \text{benzo[a]pyrene (BP)} \\
& \quad \text{a weakly carcinogenic xenobiotic} \\
\end{align*}
Detoxification strategy: Increase water-solubility to aid excretion

Detoxification backfires in people having too much cytochrome P450

Glutathione competes with DNA for BP diol epoxide