

# Benzene and Aromatic Compounds

Why is benzene so stable, and why does it react by substitution rather than addition?

●●● Intermediate

Organic Chemistry

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**Before you start:** it helps to understand [Functional Groups](#), [Reactions of Organic Compounds](#) and [Hybridization and Sigma and Pi Bonds](#).

## What is it?

**Benzene**,  $C_6H_6$ , is a ring of six carbon atoms, each bonded to one hydrogen. It is the parent of the **aromatic** compounds (arenes), a huge family that includes aspirin, paracetamol, many dyes and polystyrene.

In 1865 August Kekulé proposed a ring of **alternating** single and double bonds. But benzene does not behave like a molecule with three  $C=C$  bonds:

- all six  $C-C$  bonds are the **same length**, 139 pm, between a single bond (154 pm) and a double bond (134 pm);
- it is much **more stable** than expected;
- it does **not** decolourize bromine water, and it reacts by **substitution**, not addition.

The modern picture: each carbon is  $sp^2$  hybridized, and the six leftover p orbitals overlap side-on all around the ring. The six  $\pi$  electrons are **delocalized** above and below the ring, shared by all six carbons. This is drawn as a hexagon with a **circle** inside.

### 🔑 KEY IDEA

Delocalizing the six  $\pi$  electrons over the whole ring makes benzene unusually stable (by about 152 kJ/mol). Reactions that keep the ring intact (**substitution**) are therefore favoured over reactions that would destroy it (**addition**).

## Why does it matter?

- **Medicines and materials.** Aspirin, paracetamol, ibuprofen, many antibiotics, dyes, explosives (TNT) and plastics (polystyrene, PET) all contain benzene rings.
- **Biology.** Several amino acids (phenylalanine, tyrosine, tryptophan) contain aromatic rings, as do the bases of DNA.
- **Health.** Benzene itself is toxic and causes cancer, so it has been replaced as a solvent by methylbenzene (toluene) in most uses.

## How does it work?

### 1. Evidence from enthalpies of hydrogenation

Adding hydrogen to one C=C in cyclohexene releases 120 kJ/mol. If benzene had three separate C=C bonds, hydrogenating it to cyclohexane should release about  $3 \times 120 = 360$  kJ/mol. The measured value is only 208 kJ/mol, so benzene is about **152 kJ/mol more stable** than the Kekulé structure: the **delocalization (resonance) energy**.

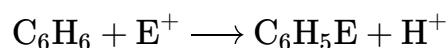
### 2. Naming aromatic compounds

| Formula                           | Name          | Common name   |
|-----------------------------------|---------------|---------------|
| $\text{C}_6\text{H}_5\text{CH}_3$ | methylbenzene | toluene       |
| $\text{C}_6\text{H}_5\text{OH}$   | phenol        | phenol        |
| $\text{C}_6\text{H}_5\text{NH}_2$ | phenylamine   | aniline       |
| $\text{C}_6\text{H}_5\text{COOH}$ | benzoic acid  | benzoic acid  |
| $\text{C}_6\text{H}_5\text{NO}_2$ | nitrobenzene  | nitrobenzene  |
| $\text{C}_6\text{H}_5\text{Cl}$   | chlorobenzene | chlorobenzene |

With two groups, number the ring carbons: 1,2- (adjacent), 1,3- or 1,4- (opposite), for example 1,4-dimethylbenzene.

### 3. Electrophilic substitution

The electron-rich ring attracts **electrophiles** (electron-pair acceptors,  $\text{E}^+$ ). An electrophile replaces a hydrogen atom, and the ring stays aromatic:



| Reaction                  | Reagents and conditions                                                          | Product            |
|---------------------------|----------------------------------------------------------------------------------|--------------------|
| Nitration                 | concentrated $\text{HNO}_3$ + concentrated $\text{H}_2\text{SO}_4$ , about 50 °C | nitrobenzene       |
| Halogenation              | $\text{Br}_2$ with an $\text{FeBr}_3$ (or Fe) catalyst                           | bromobenzene + HBr |
| Friedel–Crafts alkylation | haloalkane with an $\text{AlCl}_3$ catalyst                                      | alkylbenzene       |
| Friedel–Crafts acylation  | acyl chloride with an $\text{AlCl}_3$ catalyst                                   | aromatic ketone    |

Unlike alkenes, benzene needs a **catalyst** to react with bromine, because its stable delocalized ring is reluctant to give up its electrons.

### ∞ THINK OF IT LIKE THIS

The six  $\pi$  electrons in benzene are like six people sharing a round table instead of sitting in three fixed pairs. Shared around the whole table, everyone is more comfortable (more stable). Swapping one diner for a newcomer (substitution) keeps the table intact; breaking the table apart (addition) costs too much.

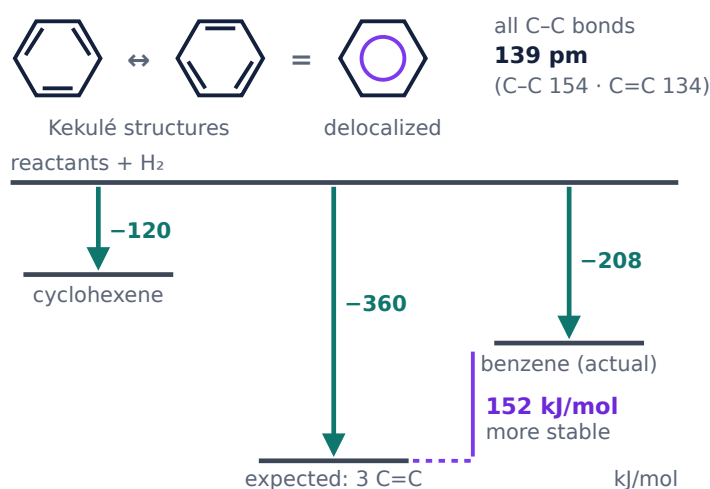
### 🔍 MORE PRECISELY

A ring is aromatic when it is planar, cyclic and fully conjugated, with  $4n + 2 \pi$  electrons (Hückel's rule; benzene has 6, with  $n = 1$ ). In nitration, the electrophile is the nitronium ion,  $\text{NO}_2^+$ , formed when sulfuric acid protonates nitric acid. Groups already on the ring change both the rate and the position of further substitution:  $-\text{OH}$  and  $-\text{CH}_3$  make the ring more reactive and direct new groups to the 2- and 4-positions, while  $-\text{NO}_2$  makes it less reactive and directs to the 3-position.

## Visualise it

### The structure and stability of benzene

Kekulé structures  $\rightleftharpoons$  delocalized ring



Benzene is more stable than three separate double bonds would suggest.

## Worked example

### WORKED EXAMPLE: The delocalization energy

**Question:** Use  $\Delta H$ (hydrogenation) of cyclohexene,  $-120 \text{ kJ/mol}$ , and of benzene,  $-208 \text{ kJ/mol}$ , to estimate how much more stable benzene is than the Kekulé structure.

**Step 1** Expected for three C=C bonds:  $3 \times (-120 \text{ kJ/mol}) = -360 \text{ kJ/mol}$

**Step 2** Difference:

$$\begin{aligned} & -208 \text{ kJ/mol} \\ & - (-360 \text{ kJ/mol}) \\ & = +152 \text{ kJ/mol} \end{aligned}$$

**Step 3** Benzene releases  $152 \text{ kJ/mol}$  **less** energy, so it is about  **$152 \text{ kJ/mol}$  more stable**.

### WORKED EXAMPLE: Alkene or arene?

**Question:** Bromine water is shaken separately with cyclohexene and with benzene. What is seen, and why?

Cyclohexene **decolourizes** bromine water quickly: bromine **adds** across the C=C. Benzene gives **no change** at room temperature without a catalyst: addition would destroy the stable delocalized ring.

### WORKED EXAMPLE: Yield of nitrobenzene

**Question:**  $7.80 \text{ g}$  of benzene is nitrated:  $\text{C}_6\text{H}_6 + \text{HNO}_3 \longrightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}$ . Calculate the theoretical yield of nitrobenzene, and the mass obtained at an  $80.0 \%$  yield.

**Step 1** Moles of benzene:

$$\begin{aligned} n &= \frac{7.80 \text{ g}}{78.11 \text{ g/mol}} \\ &= 0.09986 \text{ mol} \end{aligned}$$

**Step 2**  $1 : 1$ , so the theoretical yield is:

$$\begin{aligned} & 0.09986 \text{ mol} \\ & \times 123.11 \text{ g/mol} \\ & = 12.3 \text{ g} \end{aligned}$$

**Step 3** At  $80.0 \%$ :  $0.800 \times 12.29 \text{ g} = 9.83 \text{ g}$

## Common mistake

### **COMMON MISTAKE:** Drawing benzene as cyclohexene with three double bonds

The Kekulé structure is a useful drawing, but benzene does **not** have three short and three long bonds. All six bonds are identical; the circle notation shows the delocalized  $\pi$  electrons.

### **COMMON MISTAKE:** Expecting addition reactions

Benzene reacts mainly by **substitution**. Addition (for example, hydrogenation to cyclohexane) is possible but needs harsh conditions.

### **COMMON MISTAKE:** Forgetting the catalyst

Bromine reacts with benzene only with a halogen carrier catalyst such as  $\text{FeBr}_3$ ; nitration needs concentrated sulfuric acid to make the  $\text{NO}_2^+$  electrophile.

### **NOTATION NOTE**

- $\text{C}_6\text{H}_5^-$  is the **phenyl** group (Ph). Phenol is  $\text{C}_6\text{H}_5\text{OH}$ ; phenylamine is  $\text{C}_6\text{H}_5\text{NH}_2$ .
- “Aromatic” in chemistry means a stable conjugated ring, not a pleasant smell (though many aromatic compounds do smell).

## Remember this

### **REMEMBER THIS**

- Benzene: planar ring of 6  $\text{sp}^2$  carbons, 6 delocalized  $\pi$  electrons; all C–C bonds 139 pm.
- Evidence: equal bond lengths;  $\Delta H(\text{hydrogenation})$   $-208 \text{ kJ/mol}$  instead of  $-360 \text{ kJ/mol}$ : about  $152 \text{ kJ/mol}$  extra stability.
- Benzene reacts by electrophilic substitution, keeping the ring intact; it does not decolourize bromine water.
- Nitration: conc.  $\text{HNO}_3$  + conc.  $\text{H}_2\text{SO}_4$ , about  $50^\circ\text{C}$ . Bromination:  $\text{Br}_2$  +  $\text{FeBr}_3$ . Friedel–Crafts:  $\text{AlCl}_3$  catalyst.

## References

1. Brown, T. L.; LeMay, H. E., Jr.; Bursten, B. E.; Murphy, C. J.; Woodward, P. M.; Stoltzfus, M. W. Chemistry: The Central Science, 15th ed.; Pearson, 2022.

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