FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 9

Aromatic Hydrocarbons

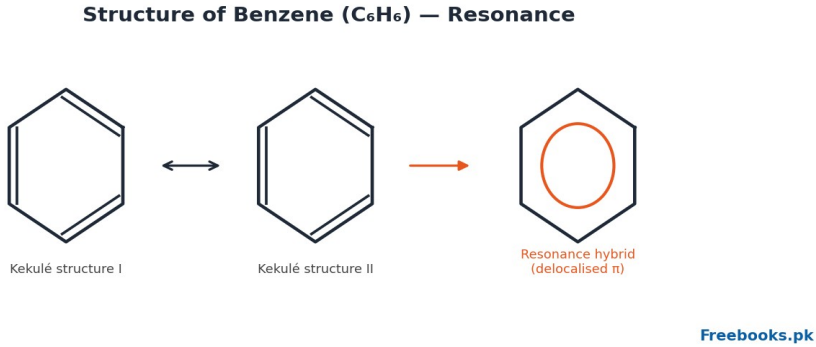

Figure 9.1 — Benzene: two Kekulé structures and the delocalised resonance hybrid.

1. Chapter Overview

Aromatic hydrocarbons are ring compounds based on benzene (C_6H_6). Although benzene is unsaturated, it does not behave like an ordinary alkene: it is unusually stable and prefers substitution reactions to addition. This special stability, called aromaticity, comes from the delocalisation of its six π-electrons around the ring. Benzene and its derivatives are hugely important, being used to make dyes, drugs, explosives, plastics and detergents. This chapter covers the structure of benzene, why it is so stable, and its characteristic reactions.

2. Learning Objectives

- Describe the structure of benzene using Kekulé structures and resonance.
- Explain aromaticity and the unusual stability of benzene.
- Explain why benzene undergoes substitution rather than addition.
- Describe the electrophilic substitution reactions of benzene (halogenation, nitration, sulphonation, Friedel–Crafts).
- Describe the addition reactions benzene can undergo under special conditions.
- State the important uses of benzene and its derivatives.

3. Key Concepts

3.1 Structure of Benzene

Benzene is a flat, six-membered ring of carbon atoms, each bonded to one hydrogen. Kekulé represented it with alternating single and double bonds, but experiments show that all six carbon–carbon bonds are identical, with a length between that of a single and a double bond. This is explained by resonance: the true structure is a resonance hybrid in which the six π-electrons are delocalised evenly around the ring (often drawn as a circle inside the hexagon).

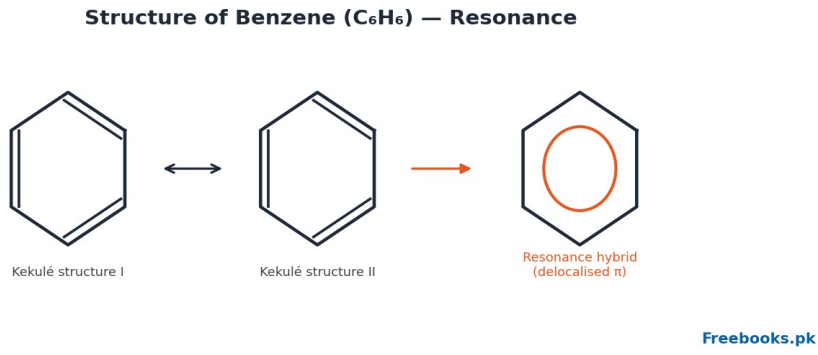

Figure 9.2 — Resonance in benzene.

3.2 Aromaticity and Stability

The delocalisation of the π-electrons lowers the energy of benzene and makes it much more stable than an imaginary molecule with three fixed double bonds. This extra stability is called

resonance (delocalisation) energy and is the reason benzene is described as aromatic. Because of this stability, benzene resists reactions that would destroy the delocalised ring.

> **Memory Trick**
> **Why substitution, not addition?** Addition would break the stable aromatic ring; substitution keeps it intact, so benzene 'protects' its ring by replacing an H instead.

3.3 Electrophilic Substitution Reactions

Benzene's characteristic reactions are electrophilic substitutions, in which an electrophile (an electron-loving species) replaces a hydrogen atom on the ring while the aromatic system is preserved. The main examples are:

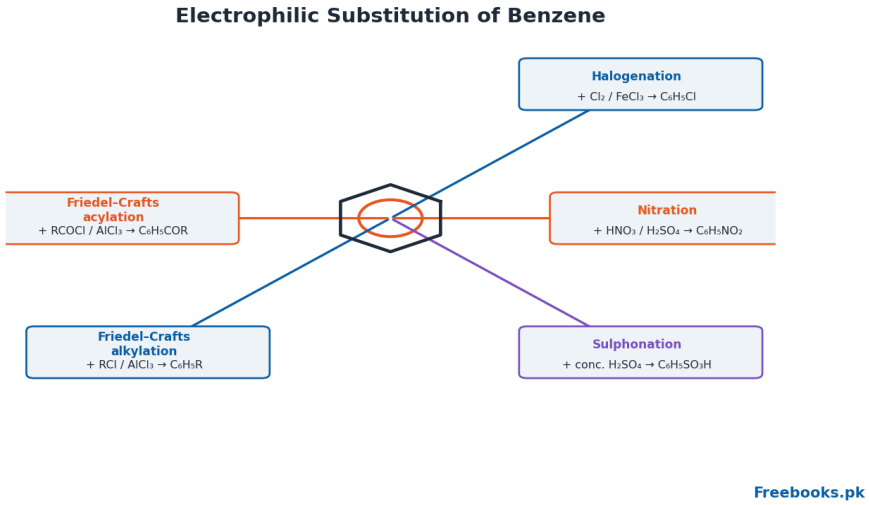

Figure 9.3 — The main electrophilic substitution reactions of benzene.

Reaction	Reagents / conditions	Product
Halogenation	Cl_2 (or Br_2) with $FeCl_3$/$FeBr_3$	Chlorobenzene, C_6H_5Cl
Nitration	conc. HNO_3 + conc. H_2SO_4, ~55 °C	Nitrobenzene, $C_6H_5NO_2$
Sulphonation	conc. (fuming) H_2SO_4	Benzenesulphonic acid, $C_6H_5SO_3H$
Friedel–Crafts alkylation	R–Cl with anhydrous $AlCl_3$	Alkylbenzene, C_6H_5R
Friedel–Crafts acylation	R–COCl with anhydrous $AlCl_3$	Aryl ketone, C_6H_5COR

> **Teacher's Note**
> Stress the common pattern: in every case an electrophile replaces one ring hydrogen, and the aromatic ring survives. Students who see the pattern can reproduce all five reactions easily.

3.4 Addition Reactions (Special Conditions)

Under forcing conditions benzene can be made to add. With hydrogen under high pressure and a nickel catalyst it forms cyclohexane, and with chlorine in bright sunlight it adds three molecules

to form benzene hexachloride (BHC, an insecticide). These reactions destroy the aromatic ring and so are much harder than substitution.

3.5 Uses

Benzene and its derivatives are used to make an enormous range of products: nitrobenzene and aniline for dyes and medicines, phenol for plastics and antiseptics, styrene for polystyrene, and detergents, explosives (TNT) and solvents. (Benzene itself is toxic and carcinogenic, so it must be handled carefully.)

4. Important Definitions

Term	Definition
Aromatic compound	A ring compound containing a benzene ring with delocalised π-electrons.
Aromaticity	The extra stability of benzene due to delocalisation of its π-electrons.
Resonance energy	The energy by which the real (delocalised) molecule is more stable than a single Kekulé structure.
Electrophile	An electron-loving species that attacks electron-rich centres.
Electrophilic substitution	A reaction in which an electrophile replaces a ring hydrogen of benzene.
Friedel–Crafts reaction	Alkylation or acylation of benzene using anhydrous $AlCl_3$.

5. Formulas / Rules

Must-Know Facts

Benzene = C_6H_6, planar ring, delocalised π-electrons (resonance hybrid).

Prefers electrophilic substitution (keeps the aromatic ring).

Nitration: conc. HNO_3 + conc. H_2SO_4 → nitrobenzene.

Friedel–Crafts: needs anhydrous $AlCl_3$ catalyst.

Addition (hard): H_2/Ni → cyclohexane; Cl_2/sunlight → BHC.

6. Diagrams / Illustrations

Key diagrams for revision:

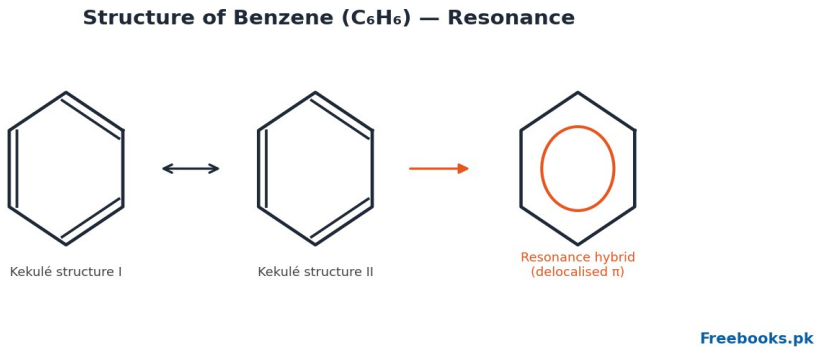

Diagram 1 — Structure and resonance of benzene.

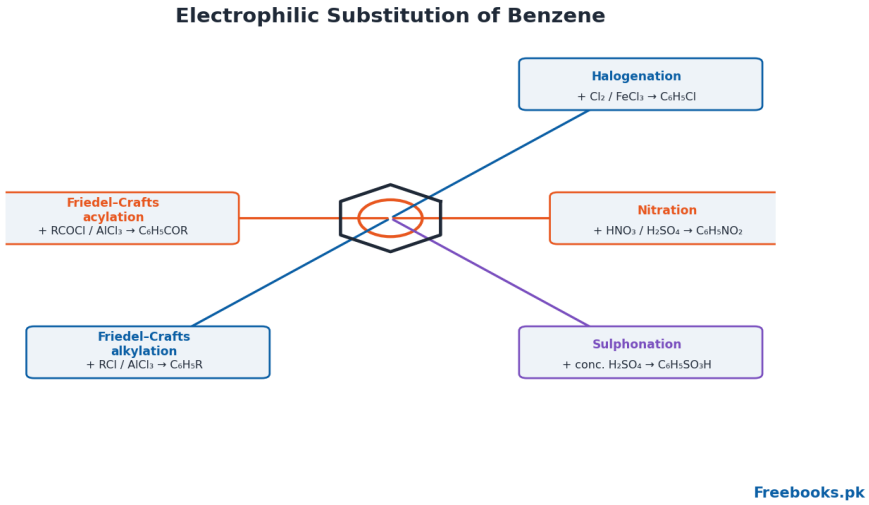

Diagram 2 — Electrophilic substitution reactions.

7. Solved Examples

Example 1 — Substitution vs addition

Q: Why does benzene undergo substitution rather than addition?

Solution: Its six π-electrons are delocalised, giving the ring extra (resonance) stability. Addition would destroy this stable ring, whereas substitution replaces a hydrogen and keeps the aromatic system intact.

Example 2 — Nitration

Q: Give the reagents and product for the nitration of benzene.

Solution: Benzene is treated with a mixture of concentrated nitric and sulphuric acids at about 55 °C to give nitrobenzene ($C_6H_5NO_2$) and water.

Example 3 — Friedel–Crafts

Q: What catalyst is required for Friedel–Crafts alkylation, and why must it be anhydrous?

Solution: Anhydrous aluminium chloride ($AlCl_3$) is required to generate the electrophile. It must be anhydrous because water destroys (hydrolyses) the catalyst, stopping the reaction.

8. Short Questions

Q1. What is the molecular formula of benzene?
Ans. C_6H_6.

Q2. What is aromaticity?
Ans. The extra stability of benzene arising from the delocalisation of its π-electrons around the ring.

Q3. Why are all C–C bonds in benzene equal in length?
Ans. Because of resonance; the π-electrons are delocalised, so every bond is identical, between a single and a double bond.

Q4. Why does benzene prefer substitution to addition?
Ans. Substitution preserves the stable aromatic ring, whereas addition would destroy it.

Q5. Give reagents for nitration of benzene.
Ans. Concentrated HNO_3 with concentrated H_2SO_4.

Q6. Name the catalyst used in Friedel–Crafts reactions.
Ans. Anhydrous aluminium chloride, $AlCl_3$.

Q7. What is formed when benzene reacts with H_2/Ni?
Ans. Cyclohexane.

Q8. Name two uses of benzene derivatives.
Ans. Making dyes/medicines (from aniline/nitrobenzene) and plastics (from phenol/styrene).

9. Long Questions

Q1. Describe the structure of benzene and explain its stability.

Benzene, C_6H_6, is a flat regular hexagon of six carbon atoms, each carrying one hydrogen. Kekulé first suggested a ring with alternating single and double bonds, but this cannot be the whole truth because measurements show that all six carbon–carbon bonds are exactly the same length, intermediate between a single and a double bond. The modern explanation is resonance: the molecule is best described as a resonance hybrid of the two Kekulé structures, in which each carbon is sp^2 hybridised and contributes one electron to a set of π-orbitals that merge into a delocalised π-cloud above and below the ring. This delocalisation spreads the electrons over all six carbons and lowers the energy of the molecule; the difference between this real energy and that of a hypothetical fixed-bond structure is the resonance energy. Because of this large resonance energy, benzene is unusually stable, which is why it resists reactions that would break up the ring.

Q2. Discuss the electrophilic substitution reactions of benzene.

Benzene reacts mainly by electrophilic substitution, in which an electron-loving electrophile replaces one hydrogen atom of the ring while the stable aromatic system is preserved. In halogenation, benzene reacts with chlorine or bromine in the presence of a catalyst such as $FeCl_3$ to give chlorobenzene or bromobenzene. In nitration, a mixture of concentrated nitric and sulphuric acids at about 55 °C introduces a nitro group to give nitrobenzene. In sulphonation, hot concentrated (fuming) sulphuric acid gives benzenesulphonic acid. In the Friedel–Crafts

reactions, anhydrous aluminium chloride is used as catalyst: alkylation with an alkyl halide gives an alkylbenzene, and acylation with an acyl chloride gives an aromatic ketone. In every case the pattern is the same — an electrophile replaces a ring hydrogen and the aromatic ring remains intact — which is why these are the characteristic reactions of benzene.

Q3. Compare the reactivity of benzene with that of an alkene.

Both benzene and alkenes are unsaturated and contain π-electrons, yet they behave very differently. In an alkene the two π-electrons are localised between two carbons; this exposed double bond is easily attacked, so alkenes readily undergo addition reactions and decolourise bromine water and $KMnO_4$. In benzene the six π-electrons are delocalised over the whole ring, giving a large resonance energy and great stability. As a result benzene does not decolourise bromine water under ordinary conditions and, instead of addition, it undergoes electrophilic substitution, which keeps the aromatic ring intact. Only under forcing conditions (H_2/Ni at high pressure, or Cl_2 in sunlight) can benzene be made to add. Thus the delocalisation of electrons makes benzene far less reactive, and differently reactive, compared with an ordinary alkene.

10. Multiple Choice Questions (MCQs)

1. The molecular formula of benzene is:
(A) C_6H_{12} (B) C_6H_6 (C) C_6H_{14} (D) C_5H_6

2. Benzene mainly undergoes:
(A) addition (B) electrophilic substitution (C) elimination (D) free-radical addition

3. The equal C–C bond lengths in benzene are explained by:
(A) isomerism (B) resonance (C) hydrogen bonding (D) catenation

4. Nitration of benzene uses:
(A) $HNO_3 + H_2SO_4$ (B) $HCl + AlCl_3$ (C) $Br_2 + FeBr_3$ (D) $H_2 + Ni$

5. The catalyst in Friedel–Crafts reactions is:
(A) $FeCl_3$ (B) $AlCl_3$ (C) V_2O_5 (D) Ni

6. Benzene + H_2/Ni gives:
(A) cyclohexene (B) cyclohexane (C) toluene (D) phenol

7. Carbon atoms in benzene are:
(A) sp (B) sp^2 (C) sp^3 (D) dsp^2

8. Benzene hexachloride is formed with Cl_2 in:
(A) dark (B) sunlight (C) $AlCl_3$ (D) water

9. Sulphonation of benzene gives:
(A) C_6H_5Cl (B) $C_6H_5NO_2$ (C) $C_6H_5SO_3H$ (D) C_6H_5OH

10. The extra stability of benzene is called:
(A) ionisation energy (B) resonance energy (C) lattice energy (D) bond energy

MCQ Answer Key

1-B 2-B 3-B 4-A 5-B 6-B 7-B 8-B 9-C 10-B

11. Quick Revision / Summary

- Benzene C_6H_6: planar ring, sp^2 carbons, delocalised π-electrons (resonance hybrid).
- Aromaticity → extra resonance stability → resists ring-breaking reactions.
- Characteristic reaction = electrophilic substitution (keeps the ring).
- Reactions: halogenation ($FeCl_3$), nitration (HNO_3/H_2SO_4), sulphonation (H_2SO_4), Friedel–Crafts ($AlCl_3$).
- Addition only under force: H_2/Ni → cyclohexane; Cl_2/sunlight → BHC.
- Derivatives → dyes, drugs, plastics, explosives.

12. Exam Tips

Teacher's Note

Always explain benzene's behaviour with 'delocalised π-electrons / resonance stability'.
Learn the five substitution reactions with reagents and catalysts in a table.
Remember catalysts: $FeCl_3$ (halogenation), $AlCl_3$ (Friedel–Crafts) — must be anhydrous.
State clearly WHY substitution is preferred over addition (keeps aromatic ring).
Nitration mixture = conc. HNO_3 + conc. H_2SO_4 — a frequent MCQ.