

Benzene structure and electrophilic substitution

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

Quick answer: Benzene, C_6H_6 , is a planar ring with six delocalised π electrons and six equal C-C bonds of 0.140 nm. Delocalisation makes it 152 kJ/mol more stable than a Kekulé triene, so benzene prefers electrophilic substitution, such as nitration, to addition reactions.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** A Level 3.3.10

What is the structure of benzene?

Benzene, C_6H_6 , is a planar ring of six carbon atoms, each bonded to one hydrogen atom. Each carbon uses one electron in a p orbital, and these six electrons form a delocalised π system above and below the ring. The ring has no separate double bonds: every C-C bond has the same length, 0.140 nm, between a single bond (0.154 nm) and a double bond (0.134 nm).

Definition

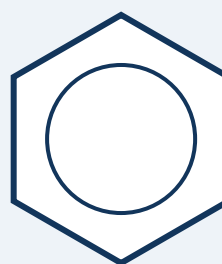
An **arene** is a hydrocarbon containing a benzene ring. **Delocalisation** is the spreading of π electrons over several atoms, which lowers the energy of the molecule. **Electrophilic substitution** is a reaction in which an electrophile (an electron-pair acceptor) replaces a hydrogen atom of the ring.



Kekulé model (not supported)

alternating C=C and C-C

≠



delocalised model

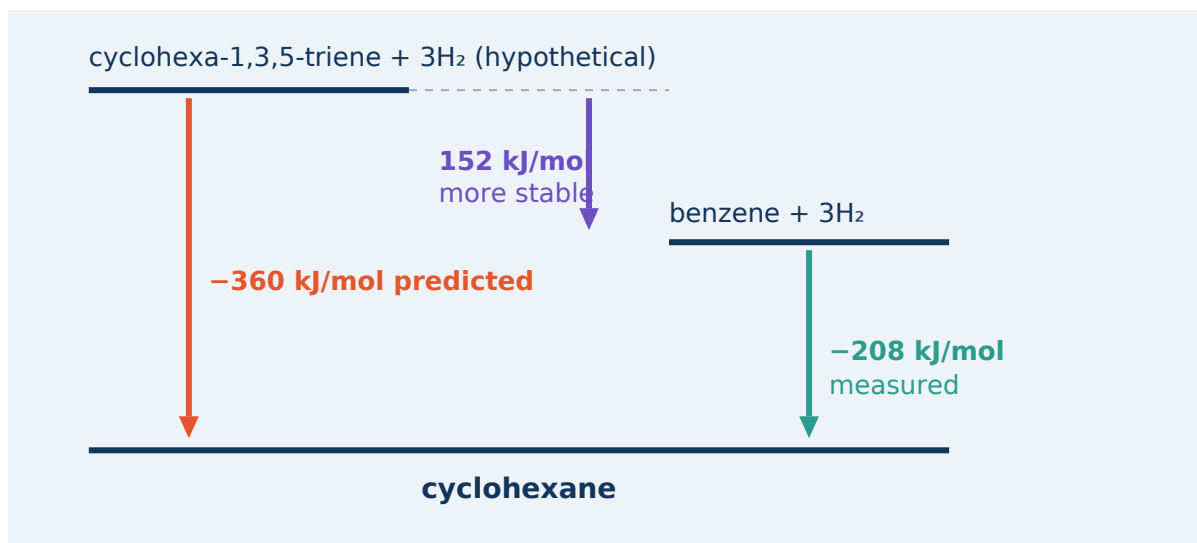
all six C-C bonds 0.140 nm, angles 120°

The ring is planar; six π electrons are spread over all six carbon atoms.

What evidence shows that benzene is more stable than a triene?

Hydrogenating one C=C bond in cyclohexene releases 120 kJ/mol. If benzene had three isolated C=C bonds, hydrogenation would release $3 \times 120 = 360$ kJ/mol. The measured value is only 208 kJ/mol. The molecule is therefore $360 - 208 = \mathbf{152 \text{ kJ/mol}}$ more stable than the

Kekulé structure suggests; this is the delocalisation energy.

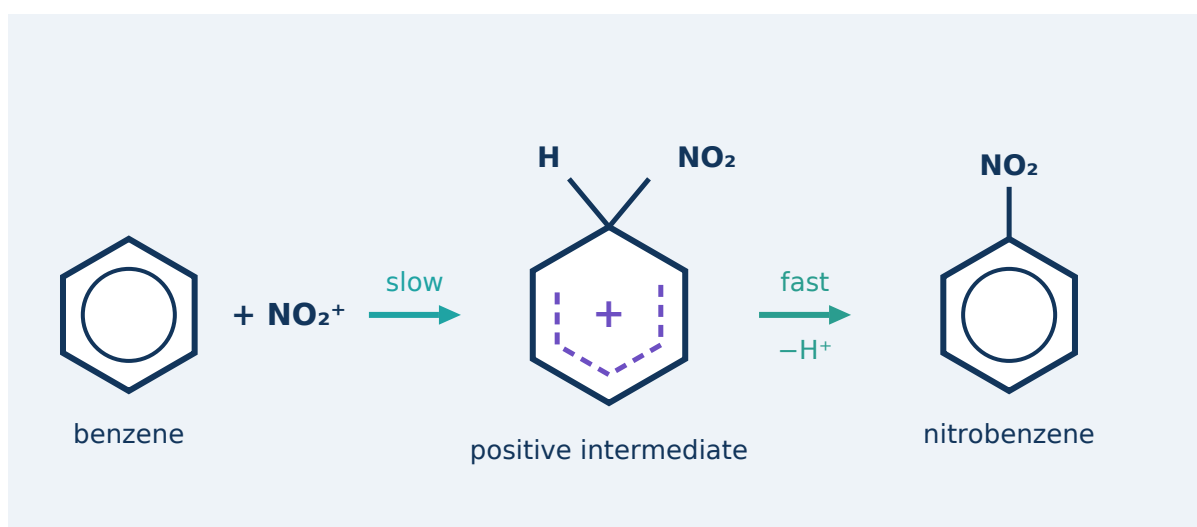


Benzene is 152 kJ/mol more stable than the localised triene would be.

The same conclusion comes from chemistry. Benzene does not decolourise bromine water, as an alkene does, and it gives only one product 1,2-dibromobenzene, whereas the Kekulé ring predicts two isomers.

How does electrophilic substitution happen?

The delocalised ring is a region of high electron density, so it attracts electrophiles. Attack on the ring temporarily breaks the delocalisation, which costs energy, so benzene reacts more slowly than an alkene and always needs a strong electrophile. The reaction ends by losing H⁺, which restores the stable ring: the result is substitution, not addition.



The first step needs the ring's π electrons to attack the electrophile; the second step restores the delocalised ring.

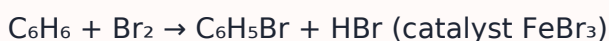
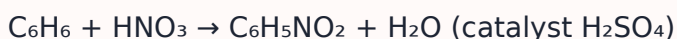
Reaction	Reagents and conditions	Product	Electrophile
nitration	conc. HNO ₃ + conc. H ₂ SO ₄ , below 55 °C	nitrobenzene	NO ₂ ⁺

Reaction	Reagents and conditions	Product	Electrophile
bromination	$\text{Br}_2 + \text{FeBr}_3$ (halogen carrier), room temperature	bromobenzene	Br^+ (polarised Br_2)
alkylation	$\text{CH}_3\text{Cl} + \text{AlCl}_3$, dry	methylbenzene	CH_3^+
acylation	$\text{CH}_3\text{COCl} + \text{AlCl}_3$, dry	phenylethanone	CH_3CO^+

Why are these reactions useful?

Each substitution attaches a functional group to the stable ring, so benzene becomes a starting material for dyes, medicines and plastics. For example, nitrobenzene is reduced by tin and concentrated hydrochloric acid to phenylamine, which is used to make azo dyes. Friedel-Crafts reactions build new C-C bonds and need dry conditions, because water destroys the aluminium chloride catalyst.

Key equations



Worked example

Use the data: $\Delta\text{H}(\text{hydrogenation})$ is -120 kJ/mol for cyclohexene and -208 kJ/mol for benzene.

Predicted for three localised C=C bonds: $3 \times (-120) = -360 \text{ kJ/mol}$.

Difference: $-208 - (-360) = +152 \text{ kJ/mol}$, so benzene is 152 kJ/mol more stable.

Worked example

Aarav nitrates 7.80 g of benzene ($M = 78.0 \text{ g/mol}$) and collects 9.84 g of nitrobenzene ($M = 123.0 \text{ g/mol}$).

Moles of benzene = $7.80 \div 78.0 = 0.100 \text{ mol}$, so the theoretical mass is $0.100 \times 123.0 = 12.3 \text{ g}$.

Percentage yield = $9.84 \div 12.3 \times 100 = 80.0 \%$.

Common mistake

Do not say benzene undergoes addition with bromine like an alkene. The ring keeps its delocalised electrons and substitutes one hydrogen with bromine, producing HBr as the second product.

Lina's tip

Remember the mechanism as three beats: make the electrophile, let the ring attack it, then lose H^+ to rebuild the ring. In mark schemes the curly arrow must start from the ring's π cloud.

Key points to remember

- Benzene: planar, C-C bonds all 0.140 nm, bond angles 120°.
- Stabilisation energy: $-360 - (-208) = 152$ kJ/mol.
- Nitration: conc. HNO_3 + conc. H_2SO_4 , below 55 °C, electrophile NO_2^+ .
- Bromination: Br_2 with FeBr_3 ; Friedel-Crafts: RCl or RCOCl with AlCl_3 .
- Mechanism: electrophile attacks the ring, then H^+ is lost to restore it.

Benzene structure and electrophilic substitution: frequently asked questions

Why does benzene not react like an alkene?

Its six π electrons are delocalised over the whole ring, which makes it 152 kJ/mol more stable. Addition would destroy this stability, so substitution happens instead.

What is the role of concentrated sulfuric acid in nitration?

It protonates nitric acid so that water can leave, forming the nitronium ion NO_2^+ , which is the electrophile. The acid is regenerated at the end of the reaction, so it acts as a catalyst.

Why is the temperature kept below 55 °C in nitration?

A higher temperature lets a second nitro group substitute, giving dinitrobenzene. Keeping the temperature low gives mostly mononitrobenzene.

What is a halogen carrier?

A halogen carrier such as FeBr_3 or AlCl_3 is a Lewis acid that polarises a halogen molecule to produce a stronger electrophile. It is regenerated at the end, so it is a catalyst.

How do you know benzene has delocalised bonds?

Its C-C bonds are all equal at 0.140 nm, its hydrogenation enthalpy is 152 kJ/mol less exothermic than predicted, it gives only one 1,2-disubstituted isomer and it does not decolourise bromine water.