3.3.10 Aromatic Chemistry

★ A-LEVEL ONLY — not examined at AS level

3.3.10.1 *Benzene: delocalised pi-system. Evidence from enthalpy of hydrogenation. Substitution preferred over addition.*

Benzene (C6H6): 6 carbons, each sp² hybridised, in a planar hexagonal ring.

Each C has one p-orbital perpendicular to the ring → sideways overlap → delocalised pi-system above and below the plane.

Evidence for delocalisation:

Enthalpy of hydrogenation of benzene is 152 kJ mol■¹ less exothermic than predicted for cyclohex-1,3,5-triene (3 isolated double bonds). This energy difference = delocalisation (stabilisation) energy.

All C–C bonds equal length (140 pm), intermediate between single (154) and double (134).

Substitution preferred over addition: addition would destroy the stable delocalised ring. Substitution preserves it.

3.3.10.2 *Electrophilic substitution: nitration (NO2+) and Friedel-Crafts acylation (AlCl3). Mechanisms.*

Nitration: C6H6 + HNO3 → C6H5NO2 + H2O. Use conc. H2SO4 + conc. HNO3 at below 55°C (above 55°C gives dinitration).

Electrophile generation: HNO3 + H2SO4 → NO2■ + HSO4■ + H2O.

Friedel-Crafts acylation: C6H6 + RCOCl → C6H5COR + HCl (AlCl3 catalyst, Lewis acid).

Electrophile generation: RCOCl + AlCl3 → RCO■ + AlCl4■.

Mechanism (both):

1. Electrophile attacks delocalised pi-system (curly arrow from ring to E■).

2. Arenium ion intermediate (ring loses aromaticity temporarily).

3. H■ lost — AlCl4■ accepts H■, AlCl3 regenerated. Ring restored.

Uses: nitration makes nitrobenzene → aniline (for dyes); acylation makes acylbenzenes (for fragrance, pharmaceuticals).