Important Concepts

The modern definition of aromaticity is the ability to sustain induced ring current by a flat or nearly flat cyclic system with (4n +2) delocalised n electrons, where n is zero or any whole number.

Benzene is the ideal molecule possessing aromaticity. It has a planar hexagonal ring structure with (4 x 1+2) or 6pie electrons. There are six p-orbitals, one on each sp? atom. All the six p electron orbitals being parallel to each other and perpendicular to the plane of the molecule, they fom a delocalised electron cloud below and above the plane. When a magnetic field is applied perpendicular to the plane of the benzene molecule the circulation of delocalized n electrons takes place in one direction and thereby a ring Current, which induces a counteraction magnetic field inside the ring, is produced (see figure). The benzene has the ability to sustain induced ring current.

Systems possessing aromaticity have some physical and chemical properties which are also collectively known as aromatic character.

i)

Chemical stability in excess of analogous acyclic unsaturated system e.g.

Although aromatic compounds have unsaturated ring, electrophilic

substitution rather than addition reaction occur and the unsaturated ring does

not get ruptured.

b) Resistance to oxidation by aqueous solution of normal oxidising agents

except group VI oxidising agents (V:0s) etc.

There are three theories regarding the cause of aromaticity:

Valence bond theory: This theory tells us that resonance stabilization of a planar cyclic structure is the cause of its aromaticity.

i)

Molecular orbital theory: According to this theory high delocalisation energy is the cause of aromaticity of planar cyclic systems.

Six p-orbitals, one form each sp C atom remain perpendicular to the plane of the hexagonal benzene ring and parallel to each other. All the six p A.O.s overlap to form six delocalised M.O's-three bonding and three anti-bonding. The three boding M.0.'s accommodate all six electrons.

The Hückel 4n2 rule: One the basis of M.O. theory Hückel stated that the presence of 4n+2 delocalized electrons in the flat or nearly flat cyclic systems is the cause of aromaticity and is known as Hückel's rule. Here n may be 0, 1, 2,3 etc., whole number. According to him 4n+2 delocalized 7-electrons of a cyclic system develop high delocalization energy or high resonance energy in it. Thus a compound to be aromatic it must be cyclic planar structure containing (4n+2) delocalized n electrons in a closed shell. This rule is applicable to monocyclic, fused ring. heterocyclic and cyclic ionic systems.

If a cyclic compound has lower n electron energy than its open chain analogue, the compound is said to be an aromatic compound.. When 1, 3, 5 hexatriene is converted to benzene by the hypothetical abstraction of two H-atoms, the n-electron energy diminishes in the system.

I

II
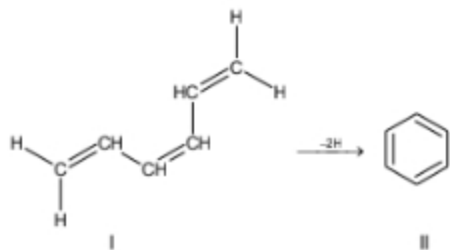
1 has more energy than 2

III

IV
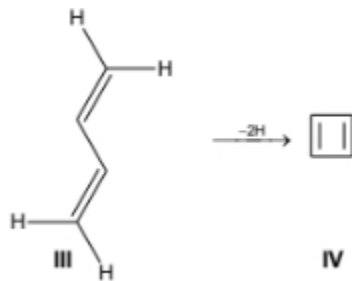
On the other hand, if a cyclic compound contains higher -electron energy than its

acyclic counterpart, the compound is called anti -aromatic, in fact planar cyclic

conjugated systems with 4n-electrons are called anti-aromatic. Hence cyclobutadiene

is an anti-aromatic compound. If in the case of hypothetical conversion of an acyclic

conjugated system into cyclic conjugated system the t-electron energy remains

unchanged the cyclic system is said to be non-aromatic.