B.Sc. (Honours) Part-III

Paper-I (General)

Topic: Aromaticity

UG
Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)

Aromaticity

Definitions:

Benzene is the simplest aromatic hydrocarbon. Aromatic compounds have unusual stability that goes far beyond what is predicted by simple resonance stabilization.

Aromaticity is defined as a property of the conjugated cycloalkenes which enhances the stability of a molecule due to the delocalization of electrons present in the π-π orbitals.

Aromatic molecules are said to be very stable, and they do not break so easily and also reacts with other types of substances. The organic compounds which are not said to be aromatic are known as aliphatic compounds. These might be in cyclic form, but only the aromatic rings have a special kind of stability.

Although the name 'aromatic' was originated from the characteristic odor or 'aroma' of benzene-like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not. Based on the analysis of a number of compounds with unusual resonance stabilization energies, the following characteristics have been accepted as criteria for aromaticity.

1. **The molecule must be cyclic, planar with uninterrupted cloud of π electrons above and below the plane of the ring.**
2. **It should have 4n+2 π electrons.**

Here every atom in the ring must have a p orbital and the delocalization should result in an uninterrupted cyclic cloud of π electrons above and below the plain of the ring. The German Chemist Erich Hückel was the first one to recognize that an aromatic compound must have an odd number of pairs of electrons, which can mathematically be written as 4n+2 (n = 0,1,2,3 etc). Molecules which obey these rules are aromatic and those which follow these rules partially fall in the category of anti-aromatic and non aromatic compounds.

The p orbital array (A) and delocalization (B) in benzene can be pictorially represented as shown below.

We will now go through examples starting from cyclopropene to higher conjugated ringsystems and look for the property of aromaticity.

Cyclopropene

1) 

Cyclopropene

2 electrons (n = 0); the delocalization is inturrupted due to sp3 methylene;
Nonaromatic

2)

Cyclopropenyl cation

2 electrons (4n+2; n = 0); the delocalization of 2 electrons is possible through the empty p orbital;
Aromatic

δ^+_____δ^+

3) **Cyclopropenyl anion**

4 electron (even number of pairs; 4n, n = 1);
Theoretically antiaromatic; not stable

Rules for Aromaticity:

1. Structure must be cyclic.

2. Each atom in the ring must have an unhybridized p-orbital.

3. The structure must be planar to allow for continuous overlap of parallel porbitals.

4. Delocalization of the π-electrons over the ring must result in a lowering of the electronic energy:

If (4n + 2)π electrons: **aromatic**

If 4n π electrons: **antiaromatic**

Non aromatic compounds, as the name implies, are not aromatic due to reasons such as lack of planarity or disruption of delocalization. They may contain 4n or 4n+2 π electrons.

Antiaromatic compounds are planar, cyclic, conjugated systems with an even number of pairs of electrons. Such compounds satisfy the first three criteria for aromaticity. i.e. they are planar, cyclic with an uninterrupted ring of p orbital bearing atoms. But they have an even number of pairs of π electrons (4n, n = 1, 2, 3 etc). It should be noted that an aromatic compound is more stable compared to an analogous cyclic compound with localized electrons, where as an antiaromatic compound is less stable compared to an analogous cyclic compound with localized electrons (in 4n+2 systems delocalization increases the stability where as in 4n systems, delocalization decreases stability)

1)

4 electrons (even number of pairs; 4n, n = 1)

Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation)

Antiaromatic

Being antiaromatic, cyclobutadiene is unstable. It can be isolated only under controlled conditions such as in Argon matrix or using trapping agents such as dienes. Studies show that it has a rectangular structure rather than a square, with C-C bond length of 1.567 Å and C=C bond length of 1.346 Å.