**AROMATICITY IN BENZENOID AND NON-BENZENOID COMPOUNDS**

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 **Aromaticity:**

 In 1931, German chemist and physicist Sir Erich Huckel proposed a theory to determine aromatic properties in a planar ring molecule. His rule states that When a cyclic, planar molecule will have **4n+2 π** electrons, it will be considered to have aromatic character. This rule is known as **Huckel rule.**

**Criteria for Aromaticity:**

1) The molecule should be cyclic (a ring of atoms)

2) The molecule should be planar/almost planar (all atoms in the molecule should lie in the same plane)

3) The molecule should be conjugated (will have **p orbitals** at every atom in the ring)

4) The molecule should be 4n+2 π electrons (where n= 01,2,3,4,…. any positive integer)

**Why 4n+2 π Electrons?**

\* According to Huckel's Molecular Orbital Theory, a compound is stable, specially, when all its bonding molecular orbitals are filled with paired electrons.

\* This is true for aromatic compounds, meaning that they are quite stable.

\* With aromatic compounds, **2 electrons** filled into the lowest energy molecular orbital, and **4 electrons** filled in each subsequent energy level (the number of subsequent energy levels is denoted by n), resulting in all bonding orbitals filled and none of anti-bonding orbitals occupied. This gives a total of **4n+2π electrons**.

 **For example,** Benzene has 6π electrons. Its first 2π electrons are filled in the lowest energy orbital, left with 4π electrons. These 4 π electrons then are filled in the orbitals of the succeeding energy level. It is observed then, how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electron.



**Method to Calculate the (4n+2 )π** electrons**:** For calculating the 4n+2 , π electrons first of all, count the number of π electronsin the molecule. Then, apply this number equal to **4n+2** and solve. If n is applicable for the values, 0 or any positive integer (1, 2, 3,...), the rule has been met.

***For example, benzene has six-π electrons: (***4n + 2 = π)

4n + 2 = 6

4n = 6 – 2

4n = 4

n = 4/4

 n = 1 , the value of n comes as 1, hence, it is aromatic.



 Thus, the molecules fulfilling the 3 characteristics listed above (***cyclic, conjugated, almost in the same plane***) and have this number of **π electrons** [4n +2] will be aromatic. The letter “**n**” is not a characteristic of the molecule because “**n**” comes from algebra and not from chemistry.

 **We must go through the each condition applicable for AROMATICITY:**

1. **Condition - 1:**The Molecule Must Be Cyclic. When this condition is met then, move to (ii) **condition -2**. (If there is no ring, the question of aromaticity will not arise)

For example, 1,3,5 hexatriene has the same number of pi bonds (and pi electrons) as benzene has, but it is not aromatic because ,no ring, no aromaticity.

 It must be kept in mind that If an Atom has 1 or more lone pair electron and is attached to an sp2 atom then this atom is also sp2 atom.





**(ii) CONDITION -2**

**Every atom in the ring must be conjugated**

Obviously, being cyclic is not the only sufficient condition for aromaticity.

 **“*Every atom in the ring must have an available p orbital*”,**

 **or**

**“*Every atom in the ring must be able to participate in resonance*”.**

 For the existence of aromaticty, there must also be a continuous ring of

 ***p*-orbitals** around the ring that build up into a larger cyclic “**pi (π) system**”.

 We must remember that the “*available* ***p orbital***” condition applies not just to atoms that are part of a **pi (π) bond**, but also atoms bearing a **lone pair**, a radical, or an empty ***p* orbital** (e.g. carbocations).

**IT MUST BE NOTED that the most important factor is presence of a sp3 hybridized atom with four bonds to atoms spoils conjugation.** Such atom cannot participate in resonance.



**(iii) Condition - 3: The Molecule Must Have [4n+2] Pi (π) Electrons**

The third condition is that the cyclic, conjugated molecule must have the correct number of **pi (π) electrons**.

**Benzene** and **Cyclooctatetraene** are both cyclic and conjugated, but benzene is aromatic and Cyclooctatetraene is not. The difference is that **benzene** has **6 pi (π) electrons**, and **Cyclooctatetraene** has **8 pi (π) electrons**. **4n+2** are not a formula which applies to see the molecule is aromatic. It is a formula that tells what numbers are in the magic series. If **pi (π) electron** value matches any number in this series then they have the capacity for “**aromaticity**.”

**The “magic series” is: 2, 6, 10, 14, 18, 22…..**

So for n = 0 , we have [4 (0) + 2] = **2**

for n = 1 , we have [4 (1) + 2 ] = **6**

for n = 2, we have [4 (2) + 2 ] = **10**

for n = 3, we have [4 (3) +2 ] = **14**

The condition that aromatic molecules must have [**4n+2**] **pi (π) electrons** is sometimes called “**Huckel’s rule**”.



**(iv) Condition - 4: The Molecule be planar or almost planar:**

The fourth condition for aromaticity is that the molecule must be flat (planar).

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**Q. Why**

**IT MUST BE NOTED : Annulenes** are monocyclic compounds containing alternating ring double bonds, such as benzene, but of different sizes. According to systematic nomenclature, **Benzene** is a [6] annulene, while **Cyclobutadiene** is [4] annulene, whereas **Cyclooctatetraene** is an [8] annulene.



 **Count pi electrons in aromatic compounds**

 **π-bonds** are simply the second bond made in a double bond. Any pure double bond is one **sigma**/**σ** and one **pi**/**π bond.** Since any one chemical bond (meaning only one line in bond line notation) contains at most **two electrons**, count

two **π-electrons** per **double bond**, and ignore the **σ-electrons**.

 If **lone pairs electron** present, consider the molecular geometry and only the **π-electrons** that are in the ring count towards aromaticity.

**Aromatic**, because 4n+2 = 6 π electrons *in the ring* (with n=1), planar,

fully conjugated all around, and cyclic.



For practice and fact check, you can see from the above examples and substantiate your answers logically-

**Aromatic**, because 4n+2=6 π electrons *in the ring* (with n=1), planar,

fully conjugated all around, and cyclic. The π electrons in the double

bond outside of the ring do **not** count towards the π electrons one

considers for aromaticity.

**Nonaromatic**, because 4n+2≠4 π electrons, where n must be an

integer. It's also not conjugated all around, so it's not antiaromatic.

The π electrons in the double bond outside of the ring do **not** count

towards the π electrons one considers for aromaticity.

**Aromatic**, because 4n+2=6 π electrons *in the ring* (with n=1), planar,

fully conjugated all around, and cyclic. The lone pair is actually in

a ***pure*** 2p orbital *perpendicular* to the ring. Don't be fooled, as the

alkyl carbon has an implicit hydrogen.

**Aromatic**, because 4n+2=6 π electrons *in the ring* (with n=1), planar,

fully conjugated all around, and cyclic. The lone pair is actually in

a ***pure* 2p orbital** *perpendicular* to the ring, which means they count

as π electrons.

**Aromatic**, because 4n+2=6 π electrons *in the ring* (with n=1), planar,

fully conjugated all around, and cyclic. Only one of the lone pairs is

actually in a ***pure* 2p orbital** *perpendicular* to the ring, which means

those counts as π electrons. The other lone pair is actually in

a **σ** (actually, ***sp2***) orbital, so it doesn't count. Thus furan is not

**Antiaromatic.**

**Huckel's Rule: Aromatic vs. Antiaromaticity**

 Antiaromaticity is a characteristic of a cyclic molecule with a **π electron system** that has higher energy due to the presence of **4n** electrons in it.

Unlike aromatic compounds, which follow Huckel's rule ([4n+2] π electrons) and are highly stable, **antiaromatic**

compounds are highly unstable and highly reactive. To avoid the instability of antiaromaticity, molecules may

change shape, becoming non-planar and therefore breaking some of the **π** interactions.

The term '**antiaromaticity**' was first proposed by ***Sir Ronald Breslow*** in **1967** as "a situation in which a cyclic delocalisation of electrons is destabilising".

**The criteria for Antiaromaticity are as follows:**

1) The molecule must be cyclic and completely conjugated

2) The molecule must be planar.

3) The molecule must have a complete conjugated π-electron system within the ring.

4) The molecule must have **4n π-electrons** where **n** is any integer within the **conjugated π-system**

**[positive integer (n = 0,1,2,3 etc.)]**.

**Predicting Aromatic & Anti-aromatic behaviour**

In the first case, the compound must be cyclic, planar (i.e. all the carbon atoms having same state of hybridization) with even number of A value.

**A= πb + e−*p* + 1(constant), *where***

**πb** = number of π bonds with in the ring system

**e-*p*** = number of electron pair outside or adjacent to the ring system i.e. if the ring contains hetero atoms (atoms containing lone pair of electrons) which can undergo delocalization and each negative charge if present may be

treated as one pair of electrons.

* **Aromatic behaviour:** If the value of ‘**A**’, for a certain organic compound comes out as **even number** then this compound will be treated as **aromatic compound**.
* **Anti-aromatic behaviour:** If the value of ‘**A**’, for a certain organic compound comes out as **odd number** then this compound will be treated as **anti-aromatic compound**.

**Order of stability** is **aromatic** > **non aromatic** > **anti aromatic**

 **Order of reactivity just follows the reverse order of stability as Anti-aromatic > non aromatic > aromatic**

**Organic Compound (Cyclic, Planar/Cyclic, non-planar)**

 **πb value [Number of π bonds with in the ring system]**

**e-p value [Number of delocalized electron pair outside or adjacent to the ring system]**

**A value [A= πb + e−p + 1]**

**Nature of the compound , ep Value.\, A= πb + e−p + 1], result**

**Benzene 3 0** A = 3+0+1 = 4 Aromatic

(Cyclic, Planar**)**

**Naphthalene 5 0** A = 5+0+1 = 6 Aromatic

(Cyclic, Planar)

**Anthracene**  **7 0** A = 7+0+1 = 8 Aromatic

(Cyclic, Planar)

**Cyclopropene**  **1 0 ,** A = 1+0+1 = 2 Non-aromatic

(Cyclic, non-planar

due to one sp3

 hybridized carbon atom)

**Cyclopropenyl cation**  **1 0 ,** A = 1+0+1 = 2 Aromatic

(Cyclic, Planar)

**Cyclopropenyl anion**  **1 1,** A = 1+1+1 = 3 Anti-aromatic

(Cyclic, Planar)

**Cyclobutadiene , 2 0,** A = 2+0+1 = 3 **Anti-aromatic**

(Cyclic, Planar)

**Cyclopentadiene** **2 0,** A = 2+0+1 = 3

Non-aromatic(Cyclic,

non-planar due to

one sp3hybridised

carbon atom)

**Cyclopentadienyl cation** (Cyclic, Planar) **2 0** A = 2+0+1 = 3 **Anti aromatic**

**Cyclopentadienyl anion** (Cyclic, Planar) **2 1** (For one negative charge on carbon whichundergo delocalization)A = 2+1+1 = 3 **Aromatic**

**Cyclooctatetraene** (Cyclic, Planar) **4 0,** A = 4+0+1 = 5 **Anti-aromatic**

**Cyclooctatrienyl cation** (Cyclic, non-planar due to one *sp3* hybridized carbon atom adjacent to positive charge), **3 0,** A = 3+0+1 = 4 **Non-aromatic**

**Pyridine (**Cyclic, Planar), **3 0 ,** (Here lone pair on N does not take part in

delocalization) A = 3+0+1 = 4 **Aromatic**

**Pyrrole , 2 1,** (Here lone pair on N take part indelocalization)

 A = 2+1+1 = 4 **Aromatic**

**Furan 2 ,** (Here out of two lone pairs on Oonly one lone pairs take part in

delocalization) A = 2+1+1 = 4 **Aromatic**

**Cyclodecapentaene, 5 0,** A = 5+0+1 = 6 **Not aromatic**

Due to the interaction of the hydrogen of 1 and 6 compound become non planar.(combination of steric and angular strain)

**Pyrene, 8 0 ,** A = 8+0+1 = 9 **Aromatic**

Because double bonded C15-C16 do not take part in resonance.

 **Which Electrons Count As π-Electrons and which types lone pair contribute to the pi (π) system?**

The total number of ***pi* (π) electrons** for the **Cyclopentadiene** anion equals 2 (from the lone pair) plus the 4 electrons in the two ***pi* (π) bonds**, giving us a total of **6**. This is a Hückel number and the Cyclopentadiene anion is in fact aromatic.

 \* For **pyrrole,** the nitrogen bears a lone pair but is not involved in a ***pi*** bond (unlike pyridine, above). Therefore it can contribute to the ***pi* (π) system** and this gives us a total of **6 pi (π) electrons** once we account for the **4** **electrons** from the **two pi (π) bonds**.

 \* In **Furan**, the oxygen bears two pairs of lone pair‟s electron, but it does not means that furan has 8 pi electrons, because each atom can contribute a maximum of one ***p*-orbital** towards the **pi (π) system**. In furan, **one lone pair**

is in a ***p* orbital**, contributing to the **pi (π) system**; the other is in the plane of the ring. This gives us a total of **6 pi (π) electrons**. Furan is aromatic. (So is thiophene, the sulfur analog of furan).

**\*Imidazole**, which has two nitrogen‟s. One nitrogen (the N-H) is not involved in a pi bond, and thus can contribute a full lone pair; the other is involved in a pi bond, and the lone pair is in the plane of the ring. This also gives us a

total of **6 pi (π) electrons** once we account for the **two pi (π) bonds**.

**Pyridine and the Benzene Anion:**

* In benzene, each ***p*-orbital** is arranged at right angles (**90°**) to the plane of the ring. Each ***p-*orbital** contains a**single electron**.
* The total number of **pi (π) electrons** in **Benzene** by counting the pi bonds: **3 pi (π) bonds** times two electrons = **6 pi (π) electrons** total.
* The **Benzene Anion** has a **lone pair** on one of the carbons. This lone pair can‟t be in a ***p*-orbital**, since the ***p*-orbital** is participating in the **pi (π) system**. Instead, it‟s at **90** degrees to the **pi (π) system**, in the plane of the ring.
* This **lone pair electron** on carbon doesn‟t count as a pair of **pi** (π) **electrons** since it can‟t overlap with the **pi (π) system.**
* **Pyridine, where the lone pair is also at right angles to the pi (π) system,** but it is participating in the **pi (π)system.**

**Aromatic Molecules:**

* **Aromatic molecules** are cyclic, conjugated, have (**4n+2**) **pi (π) electrons**, and are flat.
* **Anti-aromatic molecules** are cyclic, conjugated, have (**4n**) **pi (π) electrons**, and are flat.
* **Non-aromatic molecules** are every other molecule that fails one of these conditions.

**Some short Questions to work out-**

 Q. **What is the major difference between an antiaromatic and aromatic compound?**

(a) The structure must be cyclic for aromatic but not antiaromatic compounds.

(b) Antiaromatic compounds have **at least one *sp3* hybridized atom in the ring**

(c) Antiaromatic compound can assume a chair-like structure while aromatic compound are nearly flat

(d) Aromatic compounds cannot have a charged atom in the structure

(e) Only aromatic compounds follow **Huckle's rule**.

**Q. Why antiaromatic compounds are highly unstable?**

* Greater the delocalisation energy (resonance energy) of a compound, more stable it is. The resonance energy can be calculated using **Huckel Molecular Orbital Theory** (HMOT). Antiaromatic compounds have **zero resonance energy hence are unstable**.
* **According to HMOT,**

*Delocalisation energy =( Pi electron binding energy) - (total energy of isolated double bonds in a classical strucure)*

*Cyclopropenyl cation, Benzene, Pyrrole, Furan, Pyridine, Imidazole, Naphthalene have*

2π electrons, 6π electrons, 6π electrons, 6π electrons, 6π electrons, 6π electrons, 10π electrons respectively

 And n = 0, n = 1, n = 1, n = 1, n = 1, n = 1, n = 1

**Q. Why Cyclooctatetraene “Escapes” Anti-Aromaticity**

* Cyclooctatetraene is anti-aromatic only if it is flat. However, the relatively “**floppy**” structure of Cyclooctatetraene allows for some flexibility. The bonds can rotate away from flatness such that the molecule adopts a “tub-like” shape, thereby avoiding the “**Antiaromaticity tax**” of **18 kcal/mol** that would be paid if all the ***p*-orbitals** on the molecule were conjugated with each other.

**Q. Why Pentalene stuck in its anti-aromatic conformation**

* Pentalene (above) which also has **8 pi (π) electrons** has a very **rigid bicyclic structure** that prevents **bondrotation**away from flatness. Hence, it‟s stuck in its **anti-aromatic conformation**.

 **Points to remember while making predictions on aromaticity using Frost’s circle**

* Aromatic compounds will have all occupied molecular orbitals completely filled whereas antiaromatic compounds would have incompletely filled orbitals.
* If an antiaromatic system (4n electrons) has the freedom to undergo conformational change and become nonaromatic that would do so. Remember that antiaromatic state is less stable than aromatic and nonaromatic forms.

**Homoaromaticity**

* **Homoaromaticity**, in organic chemistry, refers to a special case of aromaticity in which conjugation is interrupted by a single ***sp3* hybridised carbon atom**.
* That means if a stabilized cyclic conjugated system (**4n+2 e s**) can be formed by bypassing **one saturated atom**, that lead to ***Homoaromaticity***.
* The concept of Homoaromaticity was pioneered by ***Sir Saul Winstein*** in 1959.

If a satisfied cyclic conjugated system [(4n+2)πe-]can be formed by passing one saturated atom that will lead to the so called Homoaromatic compound***.***

(Notes prepared as econtent for M.Sc. Chemistry students of 1st Part Paper VIth .Coutrsey-Dr. Sumant Mondal from GITAM University and Advance Organic Chemistry, Pragati Prakashan, by Pro. Jagdamba Singh)