

Hückel ($4n + 2$) Rule, Aromaticity, Antiaromaticity & Homoaromaticity



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Aromaticity : Hückel ($4n + 2$) Rule

German chemist and physicist Sir Erich Hückel (1931) proposed a theory to help determine if a planar ring molecule would have aromatic properties.

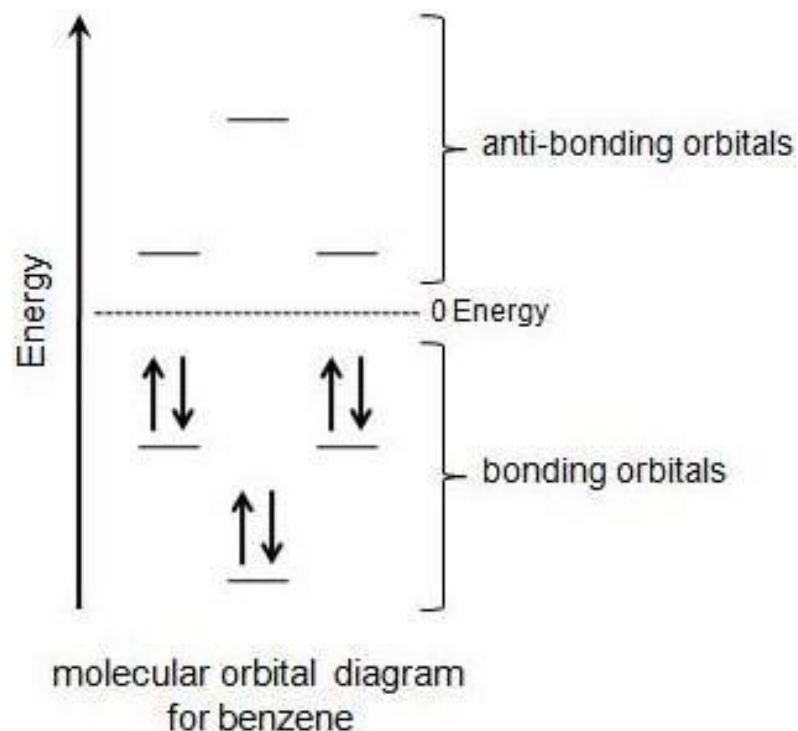
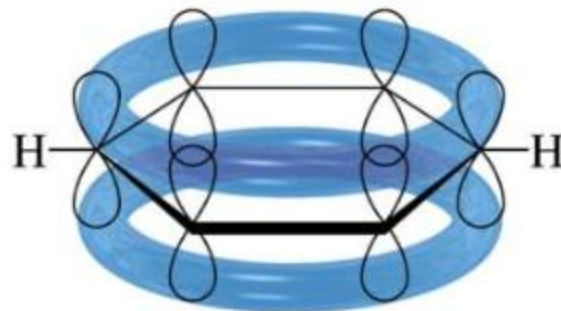
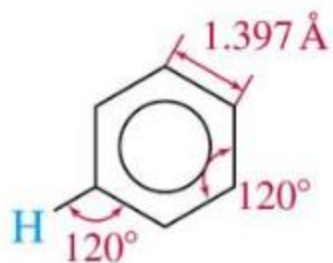
His rule states that **if a cyclic, planar molecule has $4n+2$ π electrons, it is considered aromatic.**

Criteria for Aromaticity:

- 1) The molecule has $4n+2$ π electrons ($n=0$ or any positive integer)
- 2) Cyclic (a ring of atoms)
- 3) Planar (all atoms in the molecule lie in the same plane)
- 4) Fully conjugated (p orbitals at every atom in the ring)

Why $4n+2$ π Electrons?

- ❖ According to **Hückel's Molecular Orbital Theory**, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons.
- ❖ This is true of aromatic compounds, meaning they are quite stable.
- ❖ With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving **all bonding orbitals filled and no anti-bonding orbitals occupied**. This gives a total of $4n+2\pi$ electrons.



❖ For example: Benzene has 6π electrons. Its first 2π electrons fill the lowest energy orbital, and it has 4π electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how **all of its bonding orbitals are filled**, but none of the anti-bonding orbitals have any electrons.

To apply the $4n+2$ rule, first count the number of π electrons in the molecule. Then, set this number equal to $4n+2$ and solve for n . If it is 0 or any positive integer (1, 2, 3,...), the rule has been met.

For example, benzene has six- π electrons:

$$4n + 2 = \pi$$

$$4n + 2 = 6$$

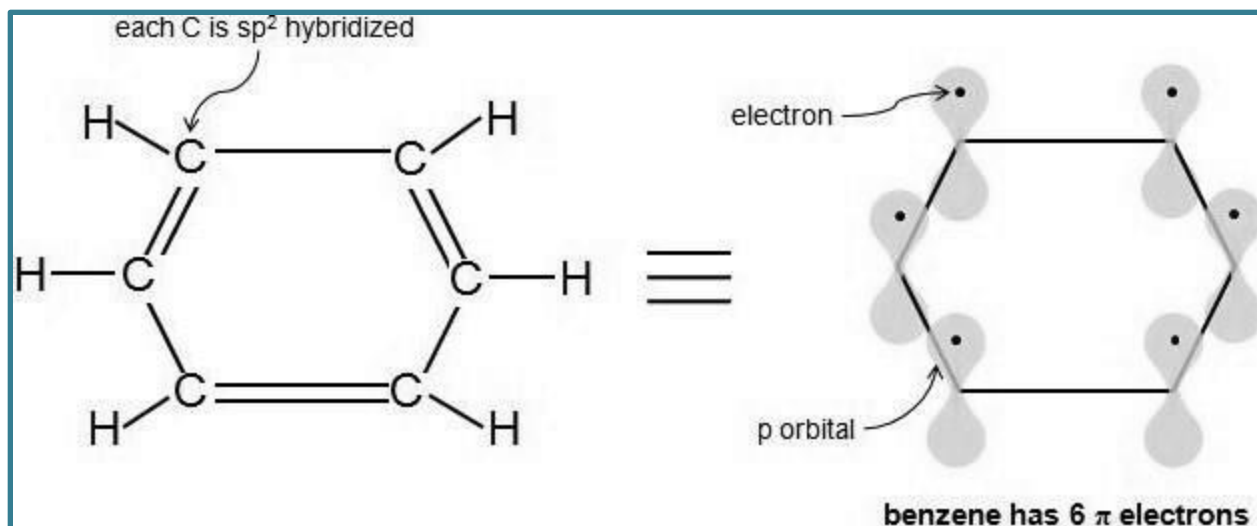
$$4n + 2 = 6$$

$$4n = 6 - 2$$

$$4n = 4$$

$$n = 4/4$$

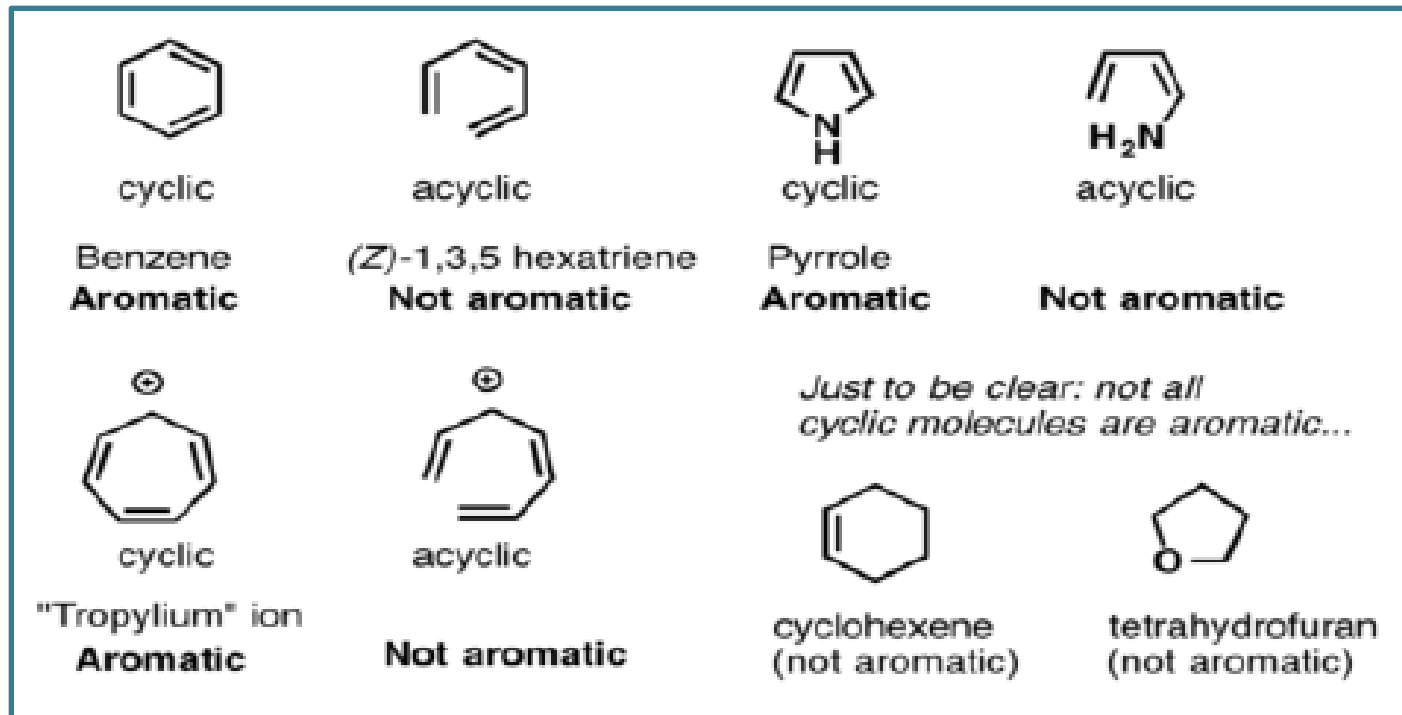
$$n = 1$$



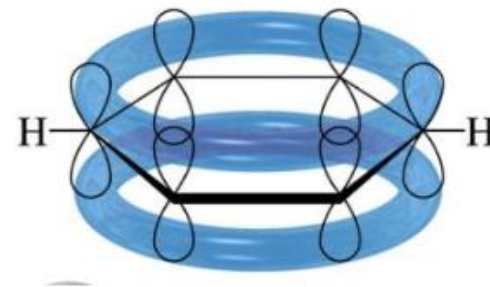
The Molecule Must Be Cyclic

Determining if a molecule is cyclic is pretty straightforward. Then, move to condition -2. **If there's no ring, forget it.**

Because as for example: (Z)-1,3,5 hexatriene has the same number of pi bonds (and pi electrons) as benzene, but isn't aromatic. No ring, no aromaticity.



Every atom in the ring must be conjugated



Obviously, **being cyclic isn't a 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”.

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

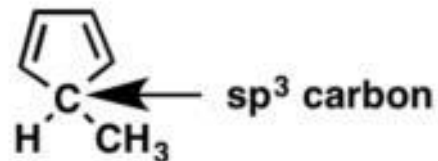
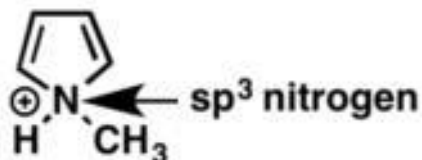
Remember that the ***“available p orbital” condition applies not just to atoms that are part of a pi (π) bond, but also atoms bearing a lone pair, a radical, or an empty p orbital (e.g. carbocations).***

NOTE: The key thing that “kills” conjugation is a *sp³ hybridized atom with four bonds to atoms. Such an atom cannot participate in resonance*

Condition #2: Every Atom In The Ring Must Be Conjugated

(alternative): every atom in the ring must have an available p orbital

(alternative): every atom in the ring must be able to participate in resonance



Aromatic

Not aromatic

Aromatic

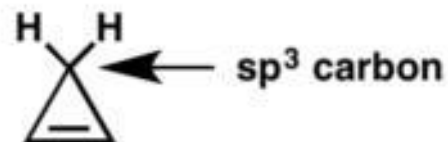
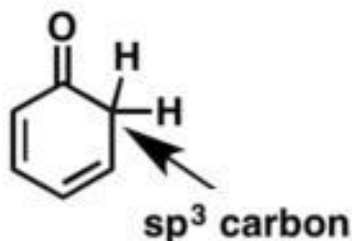
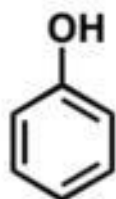
Not aromatic

*All ring atoms
conjugated*

*Nitrogen atom
is not conjugated*

*All ring atoms
conjugated*

*Carbon is not
conjugated (sp^3)*



Aromatic

Not aromatic

Aromatic

Not aromatic

*All ring atoms
conjugated*

*Carbon is
not conjugated*

*All ring atoms
conjugated*

*Carbon is
not conjugated*

an atom attached to four bonds e.g. sp^3 carbon, or nitrogen (Not aromatic)

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.

e.g. 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.

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.....

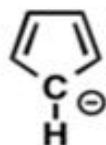
So for $n = 0$, we have $[4 (0) + 2] = 2$ for $n = 1$, we have $[4 (1) + 2] = 6$ for $n = 2$, we have $[4 (2) + 2] = 10$ for $n = 3$, we have $[4 (3) +2] = 14$

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



6 pi electrons

(fulfil Hückel's rule)



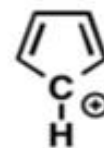
6 pi electrons

(fulfil Hückel's rule)



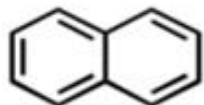
2 pi electrons

(fulfil Hückel's rule)



4 pi electrons

(do not fulfill Hückel's rule)



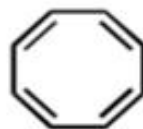
10 pi electrons

(fulfil Hückel's rule)



6 pi electrons

(fulfil Hückel's rule)



8 pi electrons

(do not fulfill Hückel's rule)



4 pi electrons

(do not fulfill Hückel's rule)



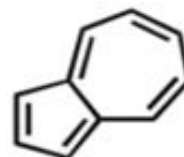
10 pi electrons

(fulfil Hückel's rule)



6 pi electrons

(fulfil Hückel's rule)



10 pi electrons

(fulfil Hückel's rule)



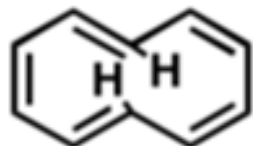
4 pi electrons

(do not fulfill Hückel's rule)

The Molecule Must Be Flat

The fourth condition for aromaticity is that the **molecule must be flat (planar)**. Aromaticity is such a stabilizing property (worth **20-36 kcal/mol**) that generally a **molecule that is**
cyclic
conjugated
has **[4n+2] pi (π) electrons**

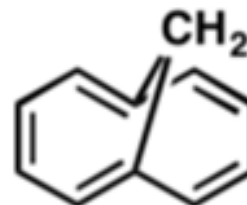
A prominent exception is the isomer of [10]-annulene below left.



not aromatic

Although it is cyclic, conjugated, and has 10 pi electrons, it is not flat due to repulsions between hydrogens that arise when it is in the flat conformation.

Since it is not flat, it is not aromatic.



aromatic !

However, replacing the hydrogens with bonds to a bridging carbon allows all C-C pi bonds to be in the same plane - aromatic!

Various examples of aromatic compounds:

1. Homocyclic aromatic compounds:

The aromatic ring contains only C atoms

e.g. benzene

2. heterocyclic aromatics

one or more of the atoms in the aromatic ring is of an element other than carbon: **oxygen, nitrogen or sulfur**

e.g. pyridine; but imidazole not only pi electrons are delocalized!!!!!!

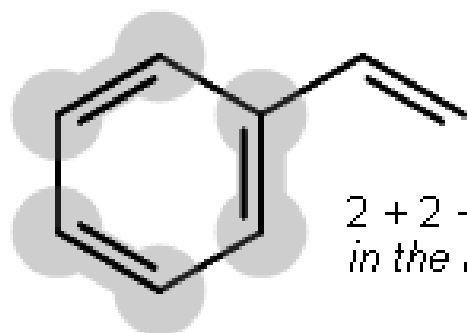
3. five-membered rings

e.g. pyrrol

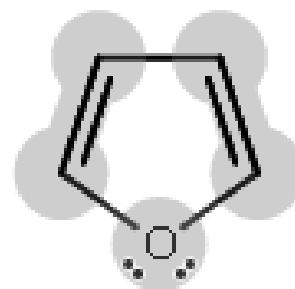
4. Polycyclic aromatic hydrocarbons :

two or more simple aromatic rings fused together by sharing two neighbouring carbon atoms

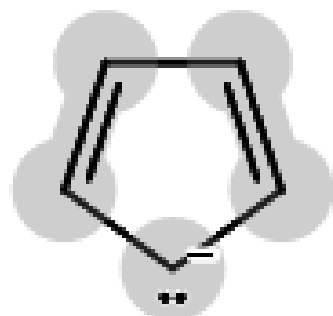
e.g. naphthalene.



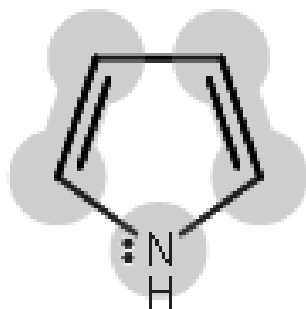
$2 + 2 + 2 = 6$ π electrons
in the ring



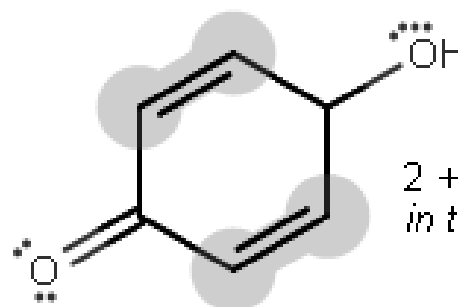
$2 + 2 + 2 = 6$ π electrons
in the ring



$2 + 2 + 2 = 6$ π electrons
in the ring



$2 + 2 + 2 = 6$ π electrons
in the ring



$2 + 2 = 4$ π electrons
in the ring

Nonaromatic, because $4n+2 \neq 4$ π electrons, where n must be an integer. It's also not conjugated all around, so it's not antiaromatic.

Huckel's Rule: Aromatic vs. Antiaromaticity

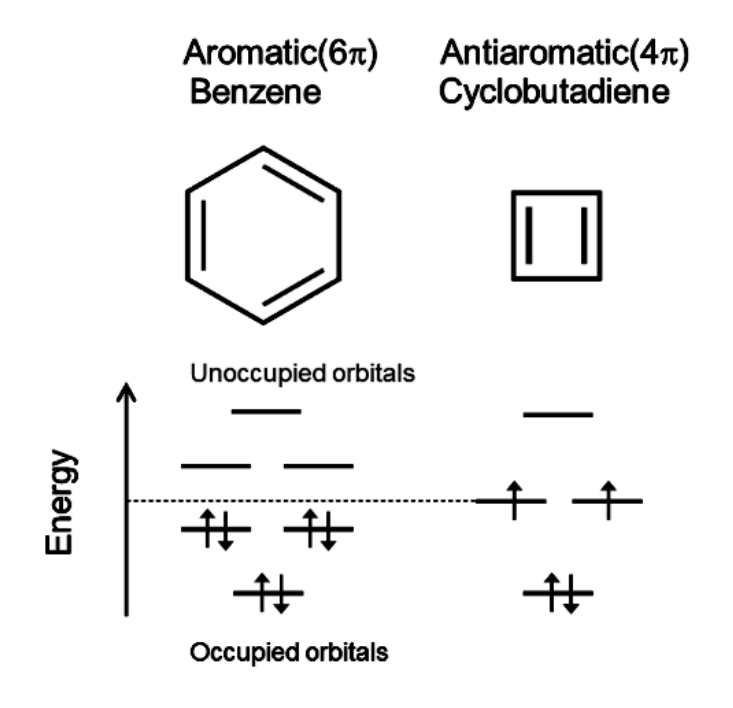
Antiaromaticity is a characteristic of a cyclic molecule with a π electron system that has higher energy due to the presence of $4n$ electrons in it.

Unlike aromatic compounds, which follow Hückel'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.)].**



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

Order of reactivity **Anti-aromatic** > **non aromatic** > **aromatic**

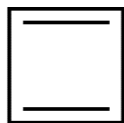
Aromatic	Anti-Aromatic	Non-Aromatic
<i>unusually stable</i>	<i>unusually unstable</i>	<i>everything else</i>
•Cyclic	•Cyclic	<i>Fails any one of the 4 criteria on the left</i>
•Conjugated	•Conjugated	
•(4n+2) Pi electrons	•(4n) Pi electrons	
•Flat	•Flat	
e.g. 	e.g. 	e.g. 
benzene (resonance energy of 36 kcal/mol)	cyclobutadiene (only stable below -100 °C)	cyclooctatetraene (adopts a tub-like shape to "escape" anti-aromaticity)

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.

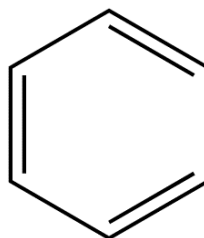
NOTE : Annulenes are monocyclic compounds containing alternating ring double bonds, such as benzene, but of different sizes. According to systematic nomenclature, Benzene is a [6] annulene, while Cyclobutadiene is [4] annulene, whereas Cyclooctatetraene is an [8] annulene.



formally [4]annulene,
better known as
cyclobutadiene

Anti-Aromatic

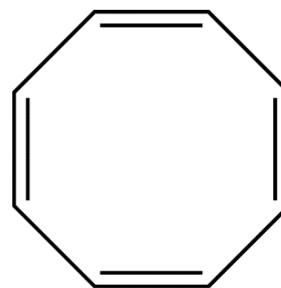
(only stable below
-100 °C)



formally [6]annulene,
better known as
benzene

Aromatic

(resonance
energy of 36 kcal/mol)



formally [8]annulene,
better known as
cyclooctatetraene

Non-Aromatic

(adopts a tub-like
shape to "escape"
anti-aromaticity)

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**.

Why antiaromatic compounds are highly unstable?

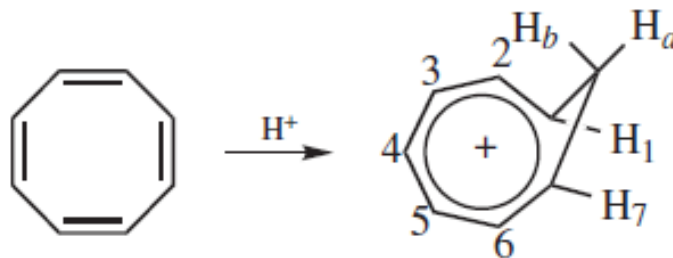
Greater the delocalisation energy (resonance energy) of a compound, more stable it is. The resonance energy can be calculated using **Huckel Molecular Orbital Theory (HMOT)**. **Antiaromatic compounds have zero resonance energy hence are unstable.**

According to HMOT,

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

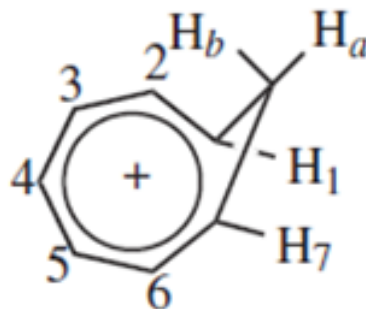
Homoaromatic Compounds

When cyclooctatetraene is dissolved in concentrated H_2SO_4 , a proton adds to one of the double bonds to form the homotropylium ion. In this species, an aromatic sextet is spread over seven carbons, as in the tropylium ion. The eighth carbon is an sp^3 carbon and so cannot take part in the aromaticity.



The NMR spectra show the presence of a diatropic ring current: H_b is found at $\delta \frac{1}{4} 0:3$; H_a at 5.1δ ; H_1 and H_7 at 6.4δ ; H_2 – H_6 at 8.5δ . This ion is an example of a **homoaromatic compound**, which may be defined as a compound that contains one or more sp^3 -hybridized carbon atoms in an otherwise conjugated cycle.

In order for the orbitals to overlap most effectively so as to close a loop, the sp^3 atoms are forced to lie almost vertically above the plane of the aromatic atoms. In Structure, H_b is directly above the aromatic sextet, and so is shifted far upfield in the NMR.



All homoaromatic compounds so far discovered are ions, and it is questionable as to whether homoaromatic character can exist in uncharged systems. Homoaromatic ions of 2 and 10 electrons are also known.

Thank You...

References:

1. <https://www.google.com>
2. <https://www.slideshare.net>