Chapter 1. Aromaticity

Chapter 2. NMR and Aromaticity

Chapter 3. Aromatic Substitution reactions

Basic concepts

Electron delocalization and resonance:

Benzene, first isolated by Michael Faraday in 1825 is the simplest and the ideal molecule to illustrate electron delocalization, resonance and aromaticity. Important milestones during structure elucidation of benzene include:

a)   Friedrich Kekule's (1866) proposal of cyclic equilibrating structures I and II   which partially explained the existence of three isomers (instead of four) for disubstituted benzene (Figure 1). If benzene is just a cyclo-triene, replacement of two hydrogen atoms by two bromines in principle should give four compounds. In realty, we will get only three, corresponding to 1,2; 1,3 and 1,4 substitutions. Kekule assumed that the two 1,2-disubstituted benzenes (III and IV) interconvert too rapidly to be distinguished.
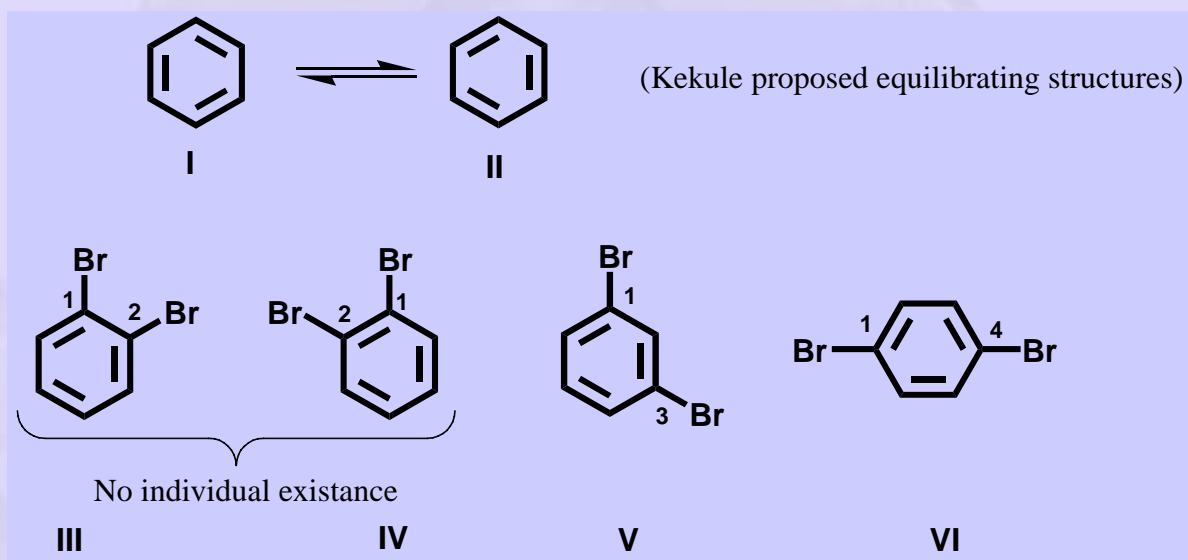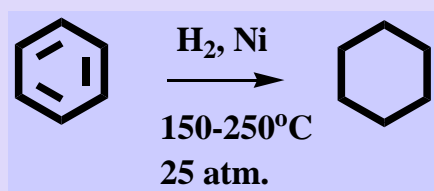

Figure 1.

b) Hydrogenation of benzene to cyclohexane by Paul Sabatier (1901) which confirmed its cyclic structure.

Debate over the structure of benzene came to an end in 1930s when X-ray and electron diffraction studies confirmed that it is a planar, regular hexagon in which all the carbon-carbon bond lengths are 1.39 Å, which is shorter than C-C single bond (1.54 Å), but slightly longer than C-C double bond (1.33 Å). Such a structure is possible only if all the carbon atoms have the same electron density, with π electrons *delocalized* over the entire skeleton of ring carbons.

Now we know that all carbon atoms in benzene are sp^2 hybridized. Each carbon atom uses two of these hybrid orbitals to form two sigma bonds with neighboring carbons and use the third orbital to form a sigma bond with 1s orbital of hydrogen. Each carbon atom has in addition a p orbital right angle to the sp^2 orbitals and planarity of the molecule allows these orbitals to overlap sideways leading to delocalization. It is now clear that benzene doesn't contains any double bonds and the exact structure is a resonance hybrid of two possible kekule structures, with delocalized electrons (Figure 2).
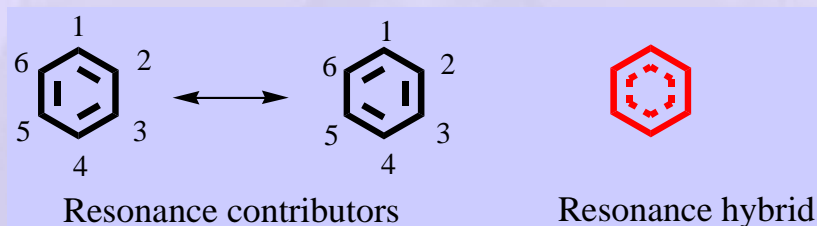

Resonance contributors   Resonance hybrid

Figure 2.
Resonance: In this, contributing structures are shown with double headed arrows separating them. This does **NOT** mean that these structures are in equilibrium with one another, but only tell that the actual structure lies somewhere in-between these contributing forms.

Delocalization is possible only if atoms sharing the electrons lie in or close to the same plane so that their p orbitals can overlap efficiently. For example, cyclooctatetraene despite having alternate single and double bonds, do not show the extended overlap of p orbitals and delocalization as it is tub shaped.
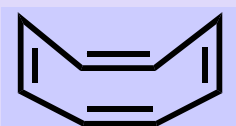
Cyclooctatetraene

Delocalization of electrons and resonance can significantly affect the properties of chemical compounds. The following are a few points worthy of special mention.

A) Rules to follow while drawing resonance structures

i)   Only electrons (π and non-bonding) move; nuclear positions remain the same
ii) The net charge in each of the contributing structures should be the same.

B) Stability and hence the contribution of individual structures to the resonance hybrid decreases if:

i)   there is an incomplete octet
ii) the negative charge is not on the most electronegative atom or the positive charge is not on the most electropositive atom
ii) there is charge separation

Take resonance structures of carboxylic acid (A&B) and carboxylate ion (C&D) for example,

A   **B**   **C**   **D**

Carboxylic acid   **Carboxylate ion**
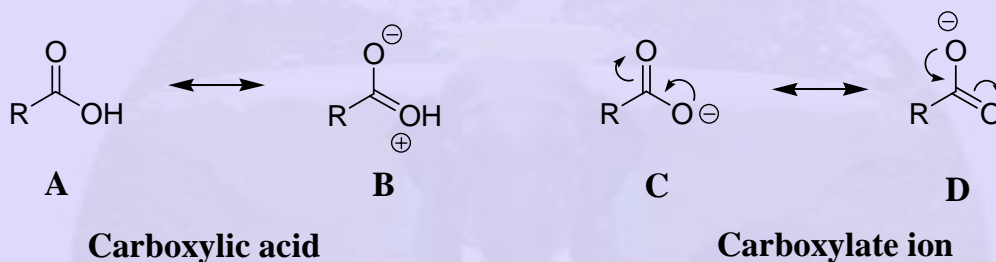
Of these, structure B has separated charges and is less stable compared to A where there is no charge separation. Hence A makes a greater contribution to the resonance hybrid of carboxylic acid. In the case of carboxylate ion, structures C & D are equally stable and contribute equally towards the resonance hybrid.

C) What really matters?

i)   The greater the predicted stability of a resonance contributor, the more it contributes to the resonance hybrid
ii) The greater the number of relatively stable resonance contributors, the greater the *resonance energy* (see below).

What is the advantage in having delocalization?

Delocalization means possibility of new orbital overlap and additional stabilization of the system. The extra stability (in terms of energy) gained through delocalization is called *delocalization energy* or *resonance energy*.

If delocalization was not possible, benzene should behave as a cyclohexatriene. Let us see how much more benzene is stable compared to this hypothetical localized structure. The heat of hydrogenation of cyclohexene has been experimentally determined to be 28.6 kcal/mol (Figure 3,A). If we consider C_6H_6 as just a cyclohexatriene, the heat of hydrogenation should be 3 x 28.6 kcal/mol = 85.8 kcal/mol (Figure 3,C). However, when the heat of hydrogenation was experimentally determined for benzene, it was found to be 49.8 kcal/mol (Figure 3,B). Since hydrogenation of cyclohexatriene and benzene both lead to cyclohexane, reason for the difference in their heat of hydrogenation should be due to the difference in their stabilities. From this, it is clear that benzene is 36 kcal/mol (ie. 85.8-49.8 kcal/mol) more stable than 'cyclohexatriene'. i.e. benzene with six delocalized π electrons is 36 kcal/mol more stable than 'cyclohexatriene' with six localized π electrons. Here, 36 kcal/mol is the resonance energy of benzene (*Heat of hydrogenation is the quantity of heat released when one mole of an unsaturated compound is hydrogenated*).
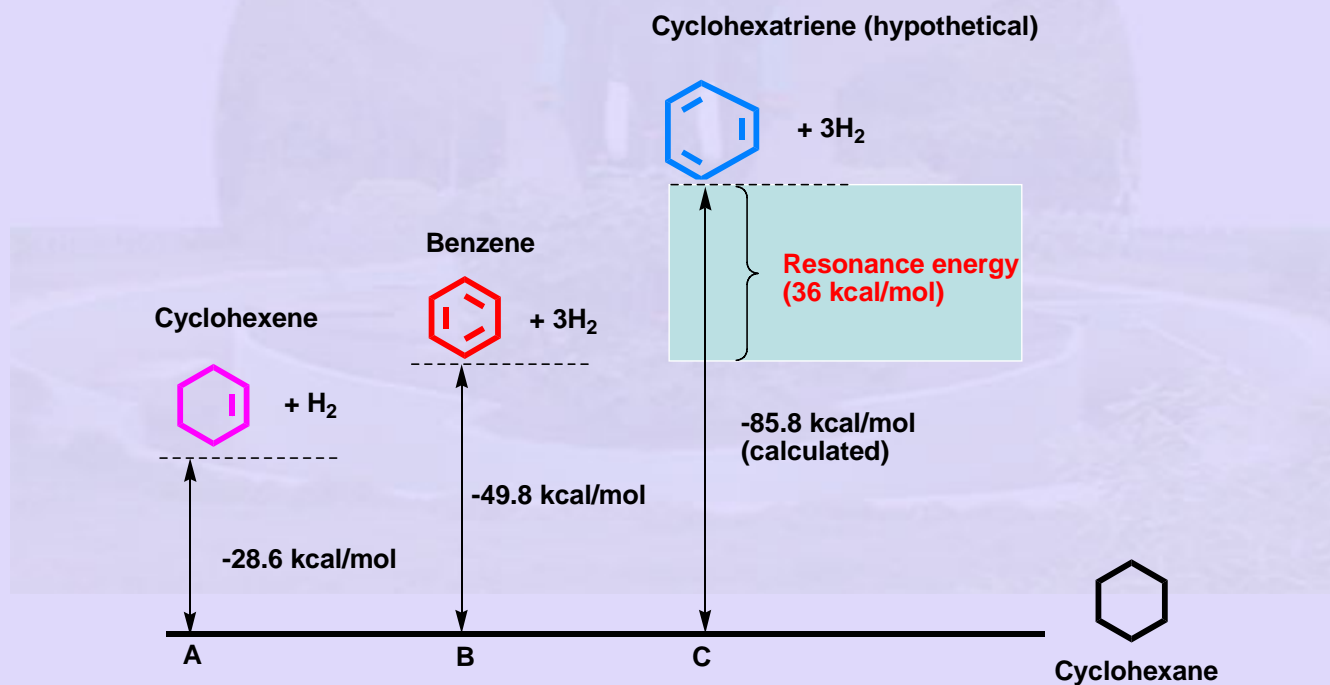

Figure 3.

Aromaticity

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 (Figure 4).
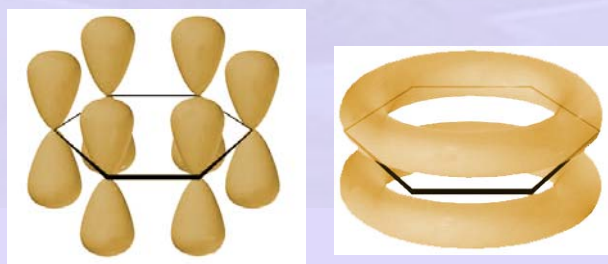

Figure 4.   A   B

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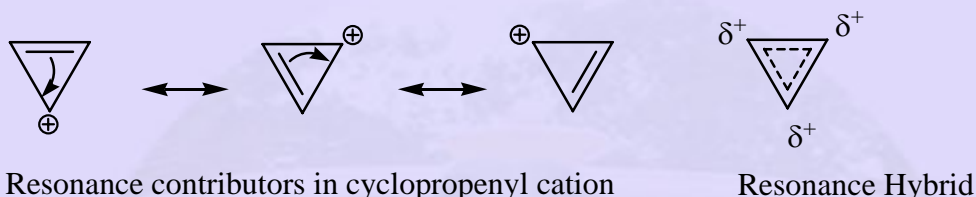
Cyclopropene

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

Resonance contributors in cyclopropenyl cation   Resonance Hybrid

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

Note:

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)*

Cyclobutadiene or [4]-annulene*

(* Monocyclic hydrocarbons with alternating single and double bonds are called annulenes. A prefix in brackets denotes the number of carbons in the ring)

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.

Br,
        Zn   (Trapping agent)   H
Br''''   H

                    > 35K
                    (no trapping agent)

            dimerise
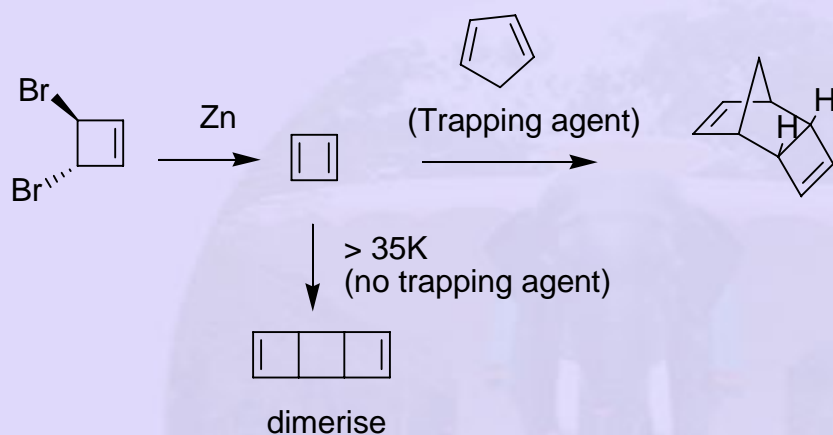
2) Cyclobutadienyl dication

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

e.g. Ionization of 3,4-dichloro- 1,2,3,4-tetramethylcyclobutene in SbF_5/SO_2 at $-75^{\circ}C$ leads to a dication whose formation and special stability is attributable to aromaticity.

H_3C CH_3 H_3C CH_3 H_3C CH_3
        Cl SbF_5 ⊕
        Cl   ⊕   ≡   ⊕
                    SO_2 ⊕
H_3C CH_3 H_3C CH_3 H_3C CH_3
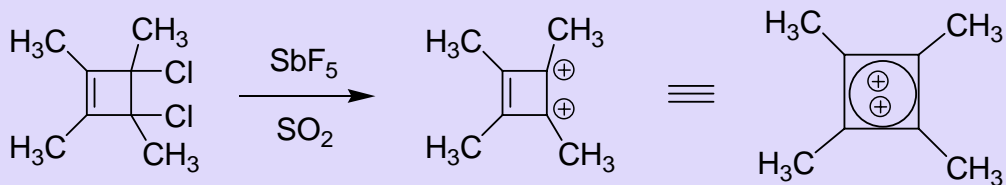
Cyclopentadiene

1)   4 electron system(even number of pairs);
Does not have an uninterrupted ring of p orbital bearing atoms (conjugation);
Nonaromatic.

Cyclopentadiene

2)   4 electron (even number of pairs; 4n, n = 1;
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation);
antiaromatic

Cyclopentadienyl cation

3)   6 electron system (4n+2, n = 1), cyclic, planar with conjugation;
Aromatic

Cyclopentadienyl anion

*The pKa of cyclopentadiene is 15, which is extraordinary for hydrogen bonded to a sp³ carbon.
The reason for this low pKa is its high tendency to become aromatic by releasing a proton.*
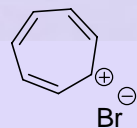
Benzene [6]-Annulene.

   A perfect example of cyclic planar molecule with uninterrupted ring of p orbital bearing atoms; 6 electron system (4n+2, n = 1)
Aromatic

## 7-membered rings- Cycloheptatriene

   Although a 6π electrom system, one of the atoms in the cyclic structure can not contribute a p orbital for conjugation.
Nonaromatic

   6π electron system, Cyclic, conjugated, planar with 4n+2 p electrons
Aromatic

Alkyl halides such as cyclopentyl chloride are nonpolar and dissolve in non-polar solvents and remain insoluble in water. Surprisingly, cycloheptatrienyl bromide is an exception. It is insoluble in nonpolar solvents, but dissolves in water! It turns out that cycloheptatrienyl bromide is an ionic compound, since its cation (known as tropylium cation) is aromatic. In the covalent form, there is no continuity in p orbital overlap as one of the carbon atoms is sp3 hybridized.

## 8 membered ring, Cyclooctatetraene or [8]-annulene
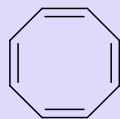
8 π electron system;
If completely planar, this molecule will become antiaromatic
(bond angle for planar structrure = 135° which can give considerable
angle strain in a cyclic structure involving sp^2 carbon atoms);
The molecule is actually boat shaped and *nonaromatic*.
(Nonaromatic form is more stable than an antiaromatic form)

1.33 Å

1.46 Å
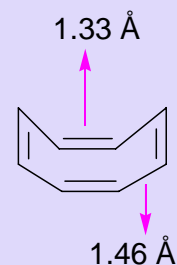
Molecular orbital description of aromaticity and antiaromaticity

Our current understanding on the structure of benzene is based on molecular orbital theory. As mentioned earlier, all the six sp^2 carbon atoms are arranged in such a way that each uses two of its hybridized orbitals to bond to adjacent carbon atoms and the third one to bond to the 1s orbital of hydrogen. The un-hybridized p orbital associated with each carbon atom contain one electron and lie perpendicular to the plane of the ring. According to molecular orbital theory, these six p orbitals combine to form six molecular orbitals, three of which are bonding and three, anti-bonding. Six π electrons occupy the bonding orbitals, which are lower in energy compared to the un-hybridized p orbitals (atomic orbitals). The relative energies of atomic orbitals and molecular orbitals are shown in Figure 5. A more comprehensive picture of electronic distribution and nodes in molecular orbitals in benzene is presented in Figure 6.
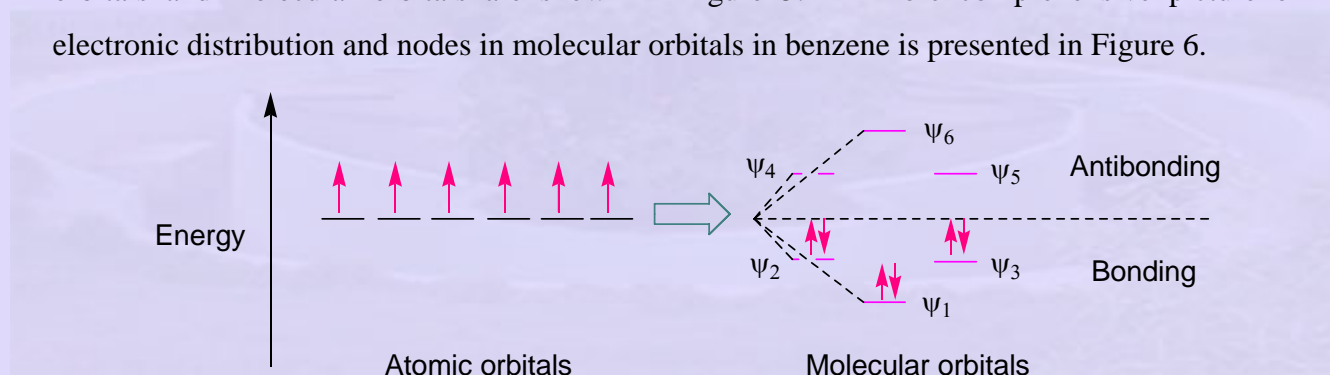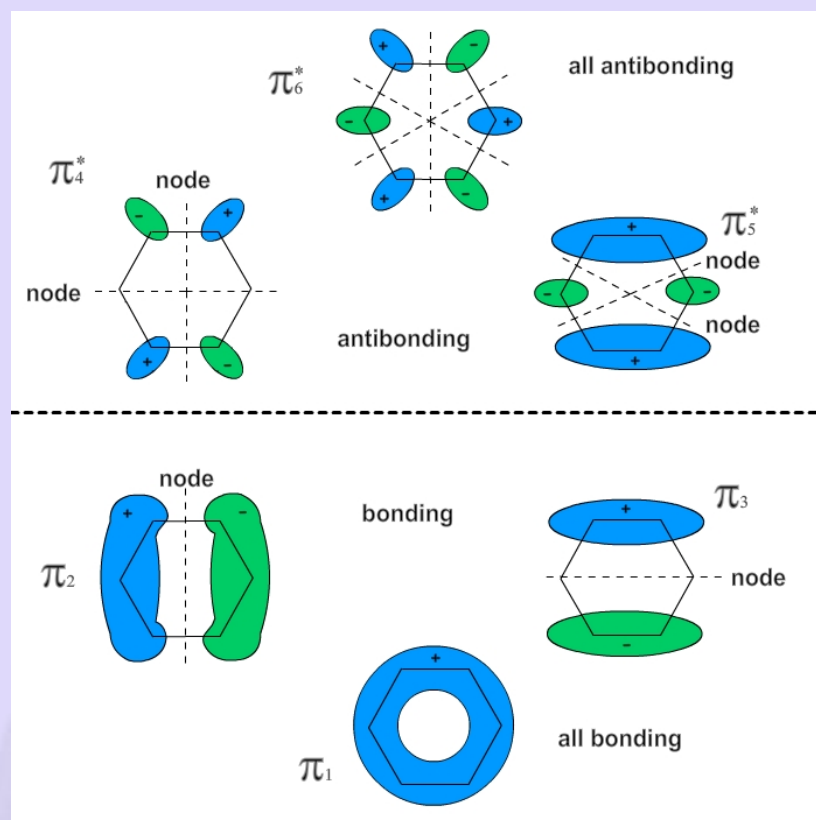
Figure 5.

Figure 6.

The relative energies of p molecular orbitals in planar cyclic conjugated systems can be determined by a simplified approach developed by A. A. frost in 1953. This involves the following steps:

1) Draw a circle
2) Place the ring (polygon representing the compound of interest) in the circle with one of its vertices pointing down. Each point where the polygon touches the circle represents an energy level.
3) Place the correct number of electrons in the orbitals, starting with the lowest energy orbital first, in accordance with Hund's rule.

If the polygon touches the circle at a horizontal diameter, that point would represent a nonbonding orbital (see illustrations below, Figure 7). Energy levels below this line indicate bonding MOs and those above are anti-bonding.

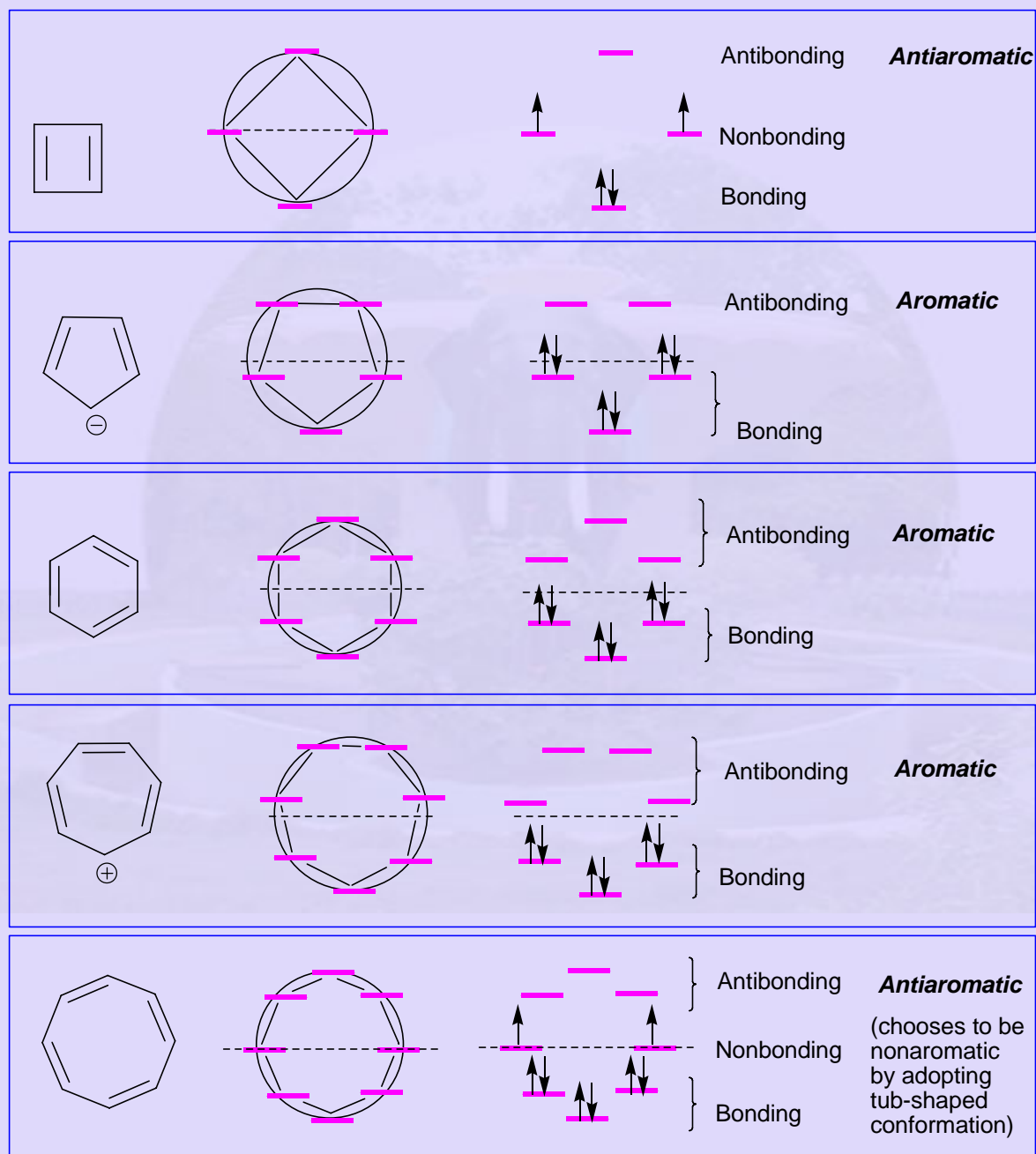**Frost diagrams - Illustrative examples**

Figure 7.

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

- Aromatic compounds will have all occupied molecular orbitals **completely filled** where as 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. A comparison of molecular orbitals in aromatic and antiaromatic systems is presented in figure 8.
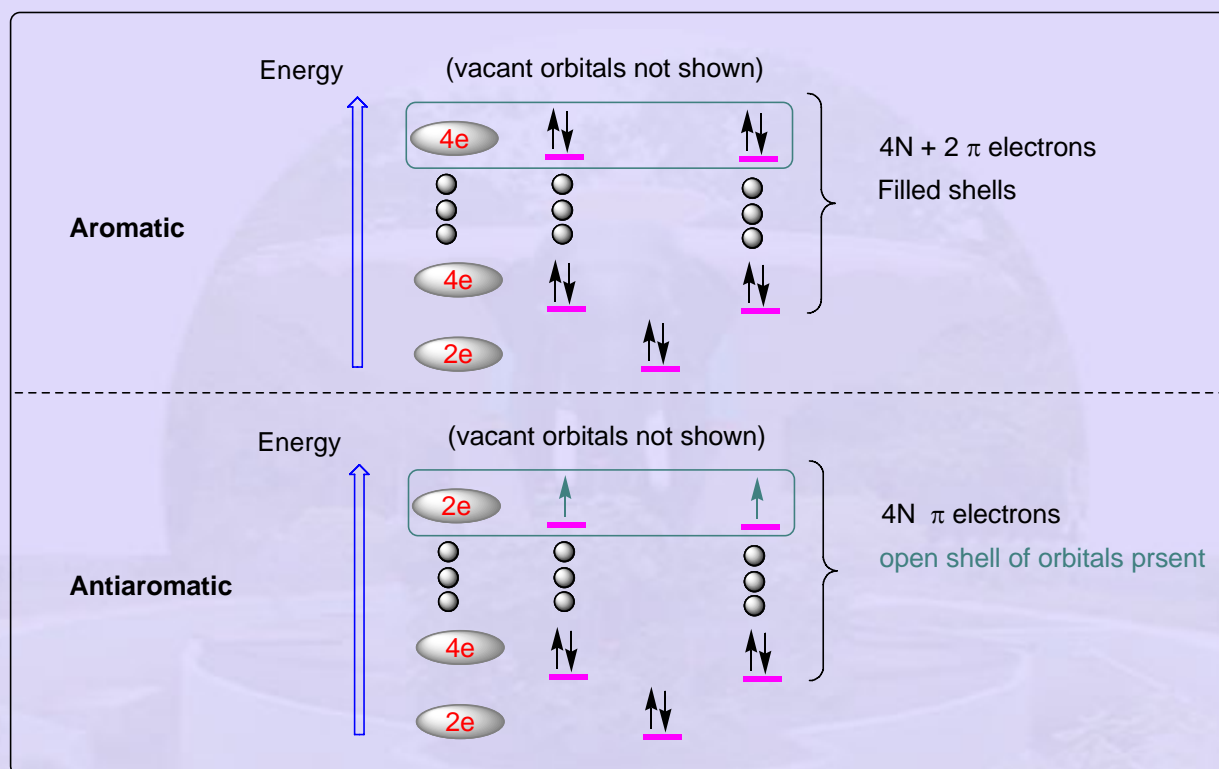

Figure 8.

Exercise: Using Frost diagrams, predict the aromatic/antiaromatic/non aromatic nature of i) cyclopropenyl cation, ii) cyclopentadienyl cation, iii) cyclobutadienyl dication, and iv) cyclooctatetraenyl dianion

Aromaticity in higher Annulenes

Completely conjugated monocyclic hydrocarbons are called annulenes.

Examples,

[4] Annulene   [6] Annulene   [8] Annulene   [10] Annulene
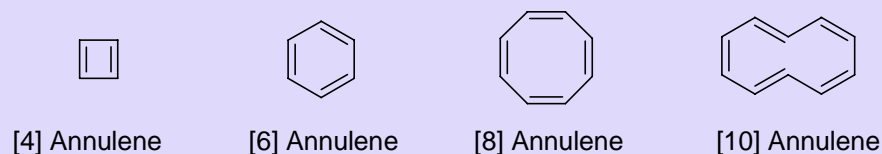
The criteria for aromaticity that we discussed earlier can be applied to higher annulenes as well. However, achieving planarity is a hurdle for many larger rings due to potential steric clashes or angle strains. If the ring (with $4n+2$ π electrons) is sufficiently large such that planarity does not cause steric or angle strains, the system would adopt that conformation, get stabilization through electron delocalization and become aromatic. Larger annulenes with $4n$ π electrons are not antiaromatic because they are flexible enough to become non-planar and become non-aromatic.

In [10]-annulene, there is considerable steric interaction between hydrogens at 1 and 6 positions. Further, a planar form (regular decagon) requires an angle of 144° between carbon atoms which is too large to accommodate in a sp2 framework. The system prefers a nonplanar conformation and is not aromatic (the fact that angle strain need NOT always be a problem in achieving planarity is evident from examples such as cyclooctatetraenyl dianion, which is stable and aromatic). Bridging C1 and C6 in [10]-annulene leads to the compound **VII** (Figure 9) which is reasonably planar with all the bond distances in the range of 1.37-1.42A^{o} and show aromaticity (In NMR, outer protons are found at 6.9-7.3 δ and the bridgehead methylene at -5.0 δ).
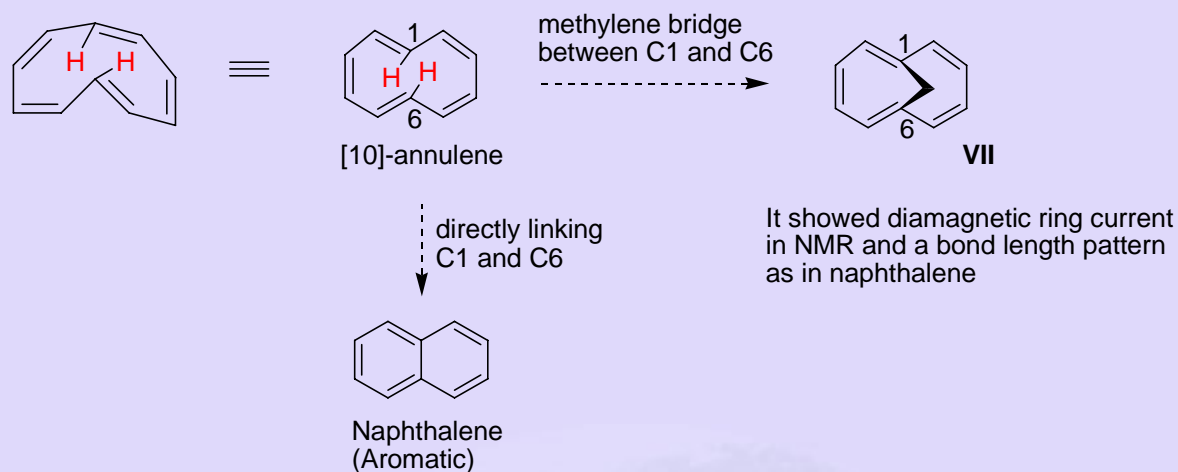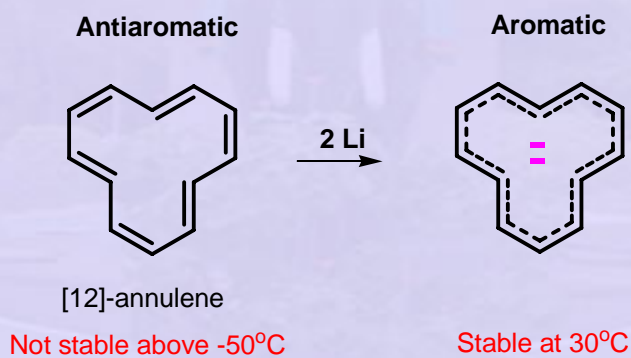
Figure 9.

[12]-annulene

[12]-annulene (4n, n = 3) is antiaromatic and hence is not stable above -50°C. Its dianion (4n+2, n = 3) is however stable up to 30°C and is aromatic (Figure 10).

(**Figure 10**).

[14]-annulene

Bond lengths in [14]-annulene range from 1.35-1.41A^o but do not show the alternating pattern of localized polyenes. It is aromatic (except for the isomers that are not planar). NMR shows that it is in conformational equilibrium as shown below (Figure 11). The steric interactions associated with internal hydrogens can be minimized if C$_3$, C$_6$, C$_{10}$ and C$_{13}$ positions are locked using suitable bridging units. Thus *trans*-15,16-dimethyldihydropyrene and its diethyl and dipropyl homologs are aromatic with C-C bond distances between 1.39-1.40 A^o. Conformational flexibility in [14]-annulene can be restricted by inserting triple bond in place of

one of the more double bonds. Here, the triple bond contributes only two electrons for delocalization leaving the other two localized.
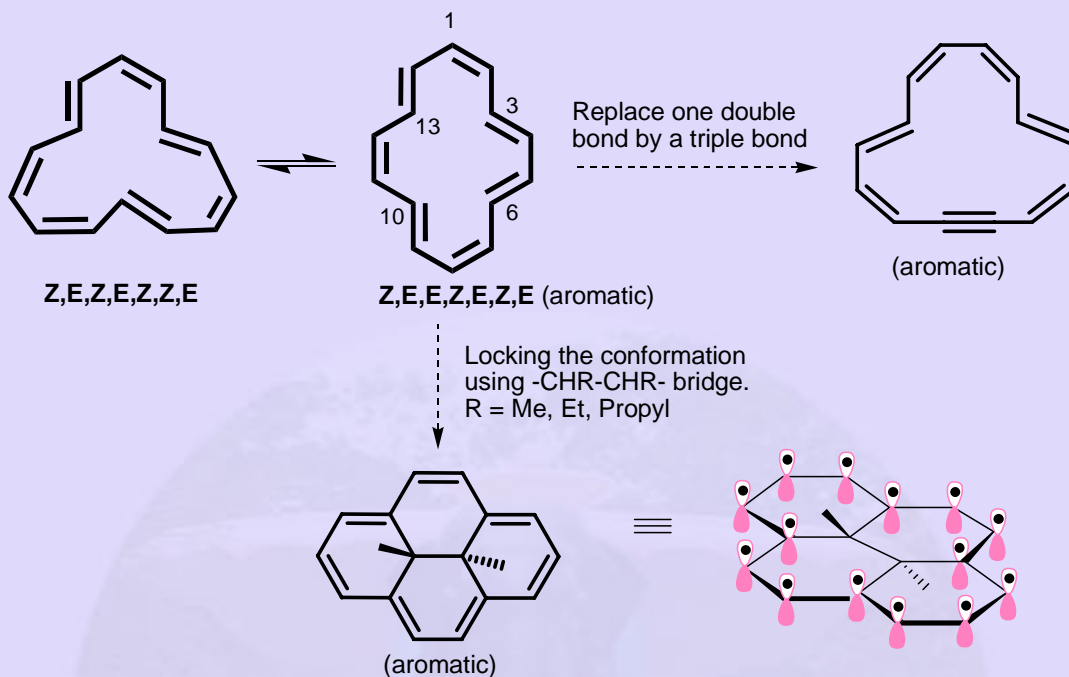

Figure 11.

[16]-annulene

[16]-annulene shows significant bond alteration, characteristic of a polyene structure (C-C, $1.46A^o$; C=C, $1.34 A^o$). It is nonplanar and is nonaromatic. Its dianion has been prepared and shows aromatic character (4n+2 system).
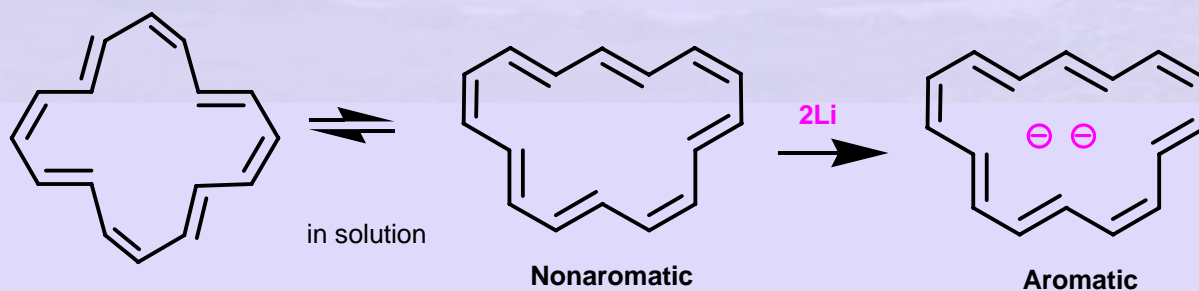

Figure 12.

[18]-annulene

The cavity in [18]-annulene is sufficiently large and hence the steric interaction involving internal hydrogens is at minimum. The molecule is free of any significant angle strain, nearly planar, and show aromaticity. Its estimated resonance energy is 37 kcal/mol, which is in the range as that of benzene. The planarity and extent of delocalization in [18]-annulene can be improved by constructing its π periphery around a saturated core as in VIII (Figure 13). This compound shows significantly improved delocalization and aromaticity (2 times) compared to [18]-annulene.
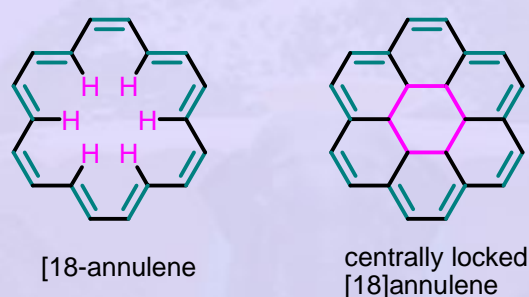

[18-annulene   centrally locked
                           [18]annulene

Figure 13.

Homoaromaticity

If a stabilized cyclic conjugated system (4n+2 e s) can be formed by bypassing one saturated atom, that lead to homoaromaticity. Compared to true aromatic systems, the net stabilization here may be low due to poorer overlap of orbitals. Cyclooctatrienyl cation (homotropylium ion) formed when cyclooctatetraene is dissolved in concentrated sulfuric acid is the best example to demonstrate homoaromaticity. Here, six electrons are spread over seven carbon atoms as in Tropylium cation. Electron delocalization in this case is pictorially represented below (Figure 14).
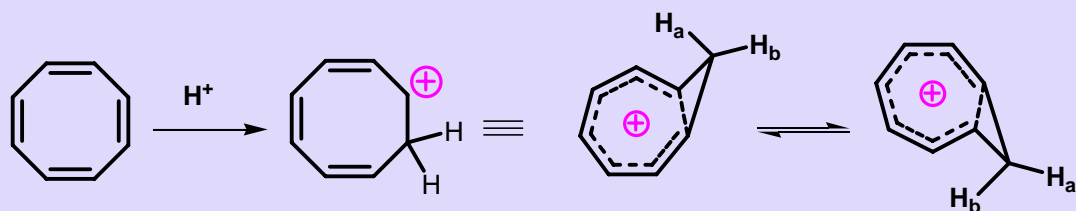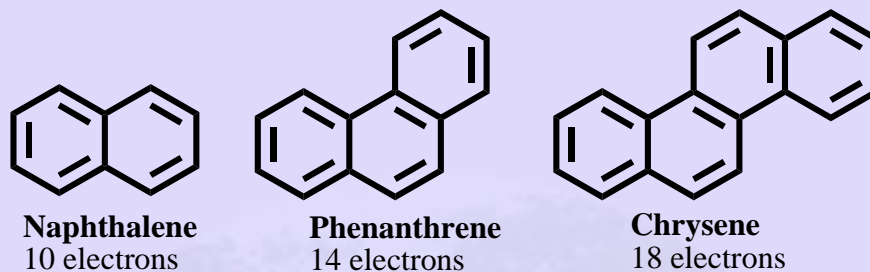

**Figure 14**.

Aromaticity in fused rings

The criteria for aromaticity in mono cyclic hydrocarbons can be applied for polycyclic hydrocarbons as well. Following are some of the well known examples for this class of compounds.

Naphthalene
10 electrons

Phenanthrene
14 electrons

Chrysene
18 electrons

As the number of aromatic rings increases, the resonance energy per π electron decreases. As a result, larger polynuclear aromatic hydrocarbons have a tendency to undergo addition reaction to an internal ring to give more stable compounds.

(mixture of cis and trans isomers)
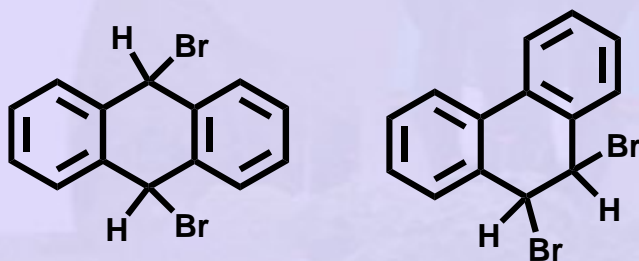
Azulene is one of the few non-benzenoids that appears to have significant aromatic stabilization. It has a noticeable dipole moment (0.8 D). It acts like a combination of cyclopentadienyl anion and cycloheptatrienyl cation. In contrast, Pentalene and heptalene which posses fused five and seven membered rings respectively are not stable as expected on the grounds of antiaromaticity. Attempted synthesis of the former led to the formation of a dimmer, where as the latter undergo polymerization. It is interesting to note that the conjugate acid of heptalene is very stable, reflecting the stability of resulting Tropylium cation.

Azulene   Pentalene   Heptalene

unstable, readily dimerises

H+
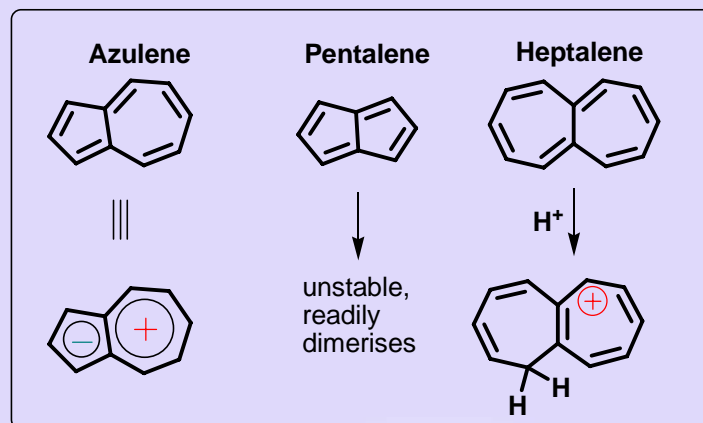
Fulvalenes represent another interesting class of compounds to look for potential aromaticity. Among possible symmetrical structures, pentafulvalene and heptafulvalene have been prepared, but were found to exhibit polyene character. However, when a combination of rings, such as cyclopentadiene and cyclopropene were examined, results were in support of the existence of dipolar resonance structures. The large measured dipole moments of phenyl substituted analog x and reduced barrier of rotation (as revealed by NMR) of the dialkyl substituted analog x' are manifestations of such effects.

triafulvalene   pentafulvalene   heptafulvalene

μ = 6.3D