Aromaticity in Organic Compounds

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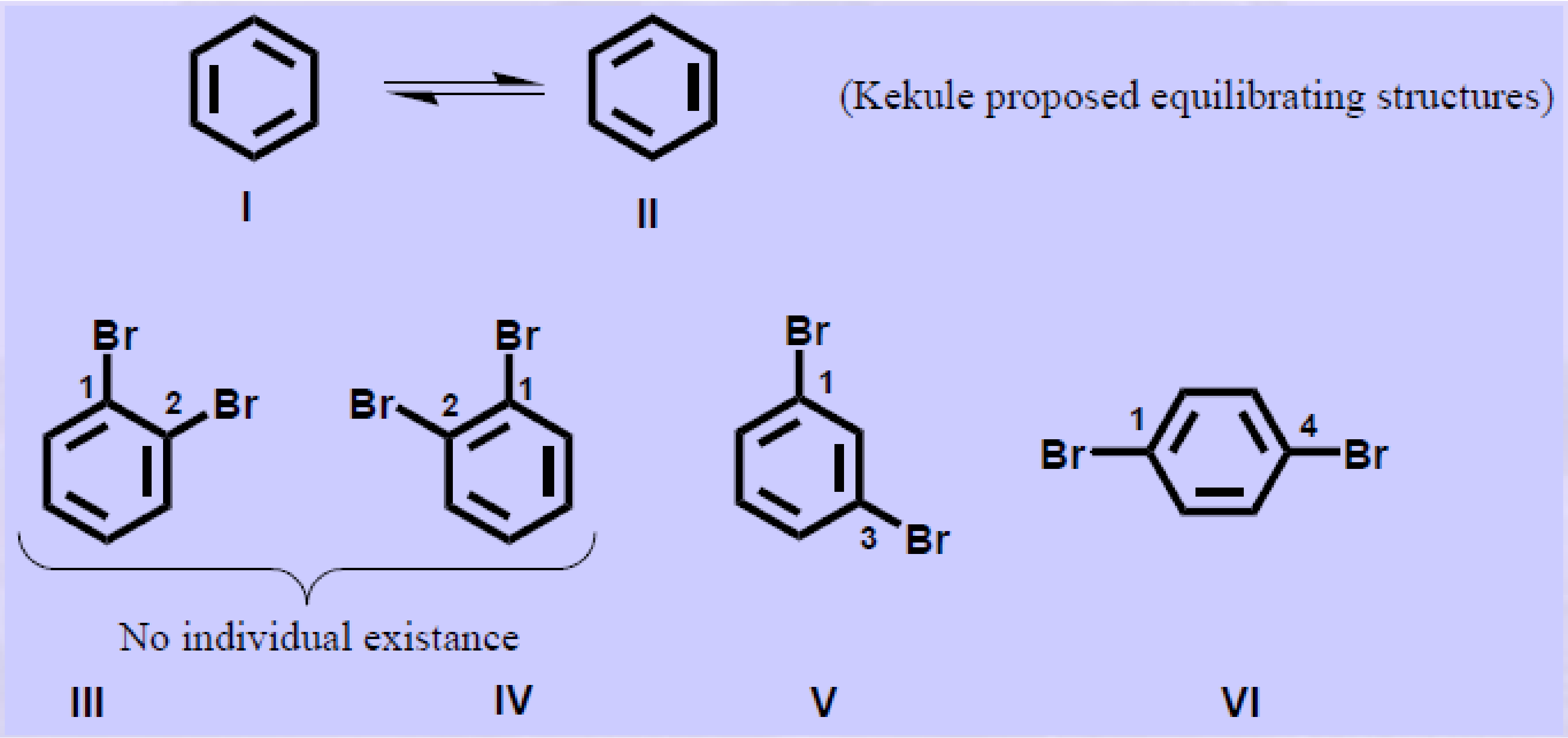
Structure of Benzene

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 !!!

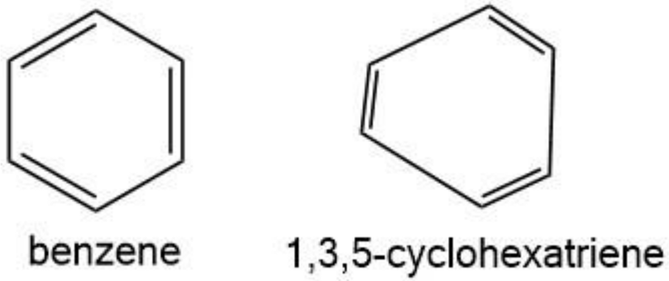


I II

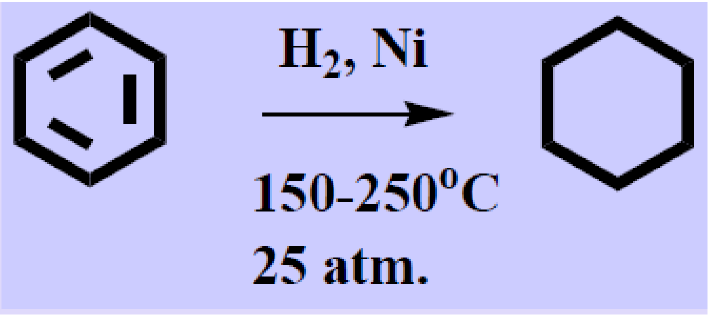
(Kekule proposed equilibrating structures)

No individual existance

III IV V VI



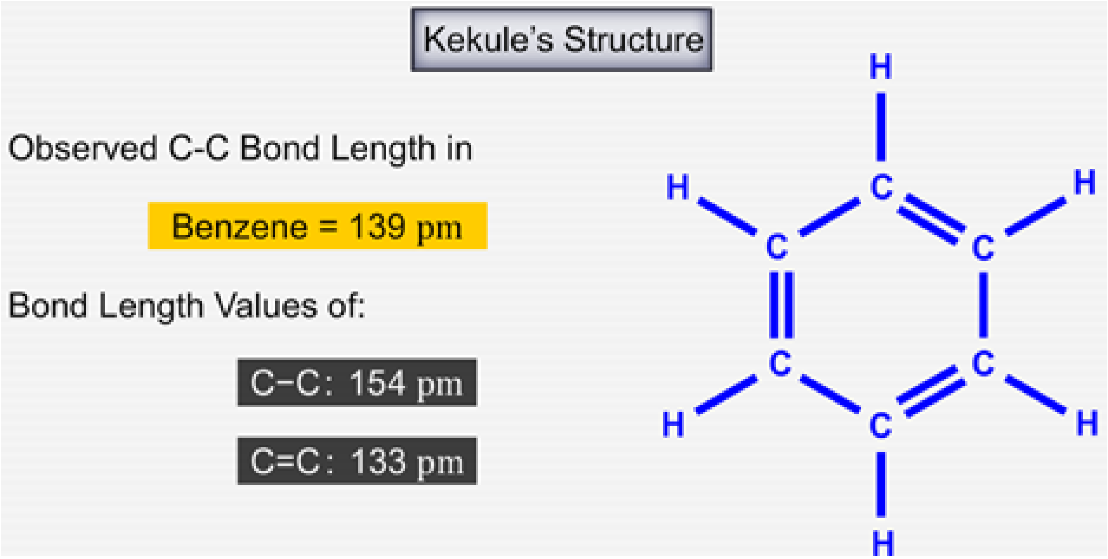
benzene 1,3,5-cyclohexatriene



$\xrightarrow[\text{150-250}^{\circ}\text{C, 25 atm.}]{H_2,\ Ni}$

Paul Sabatier (1901)

Structure of Benzene



Kekule's Structure

Observed C-C Bond Length in

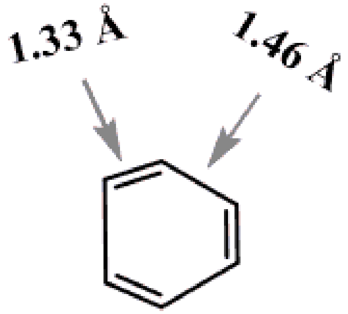
Benzene = 139 pm

Bond Length Values of:

C−C: 154 pm

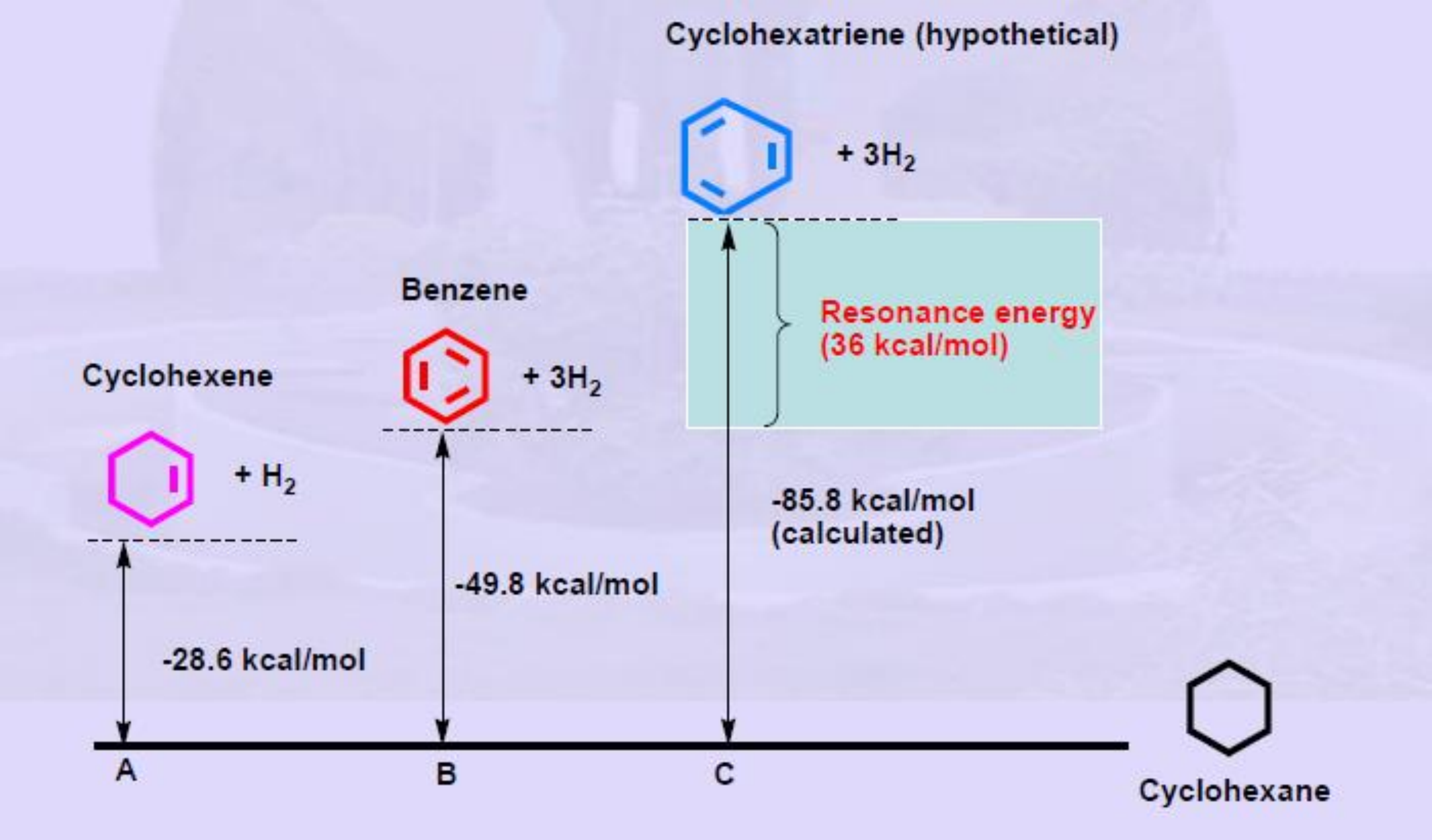
C=C: 133 pm

short bond
(exaggerated)



long bond
(exaggerated)

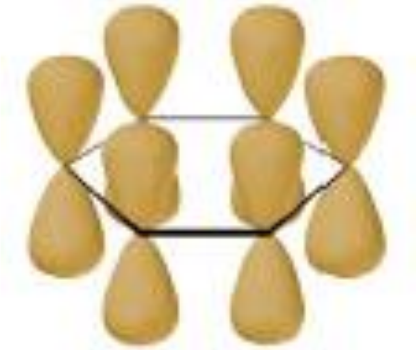
Stability of Benzene: Resonance Energy



What is Aromaticity ?

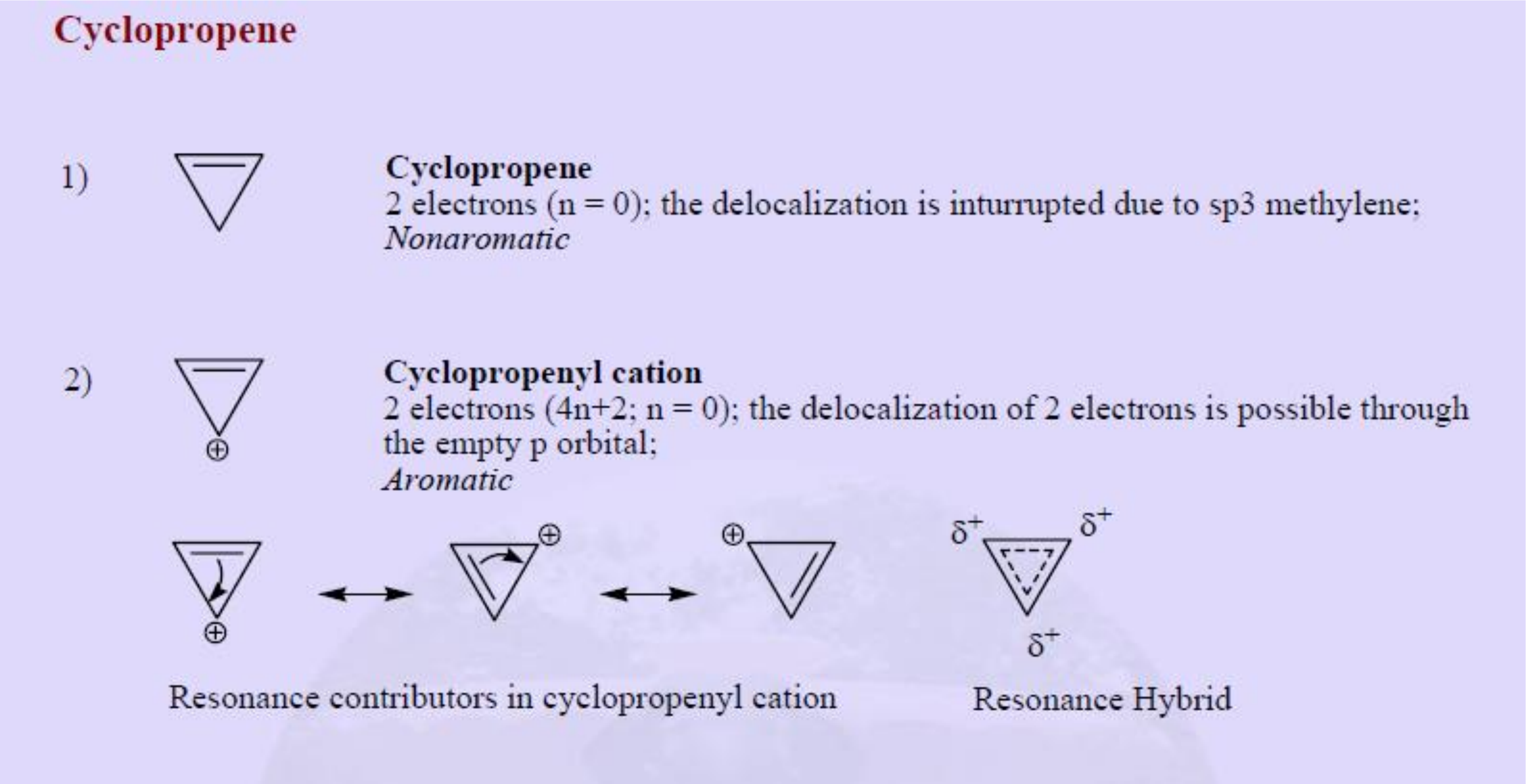
Although the name ‘aromatic’ was originated from the characteristic odor or ‘aroma’ of benzene-like compounds, chemists now have a completely different method of deciding whether a compound is aromatic or not. Based on the analysis of a number of compounds with unusual resonance stabilization energies, 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.**

Aromaticity in rings of different sizes



Cyclopropene

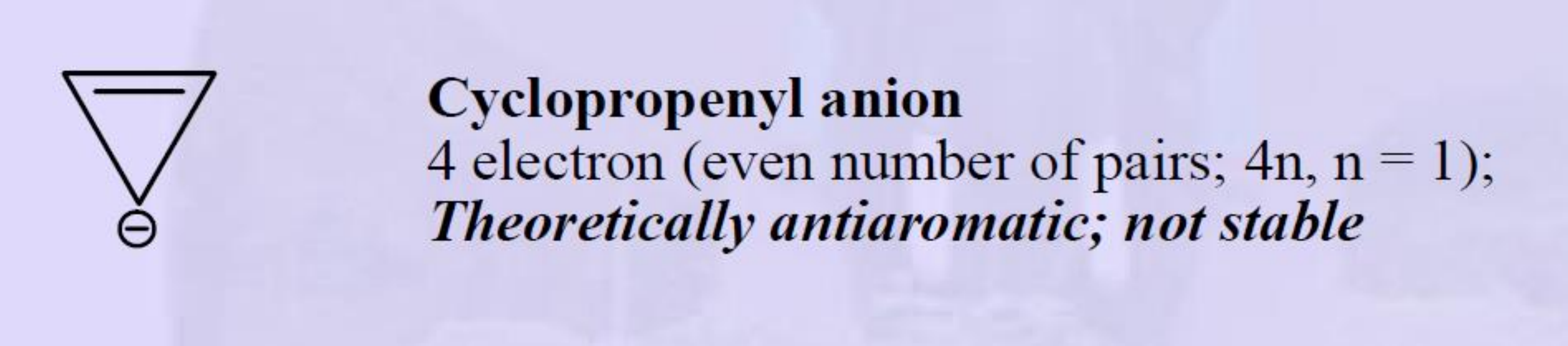
1) **Cyclopropene**
2 electrons (n = 0); the delocalization is inturrupted due to sp3 methylene;
Nonaromatic

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

Non-aromatic and Anti-aromatic Compounds



Cyclopropenyl anion

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

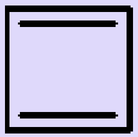
Theoretically antiaromatic; not stable

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.

Anti-aromatic 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).

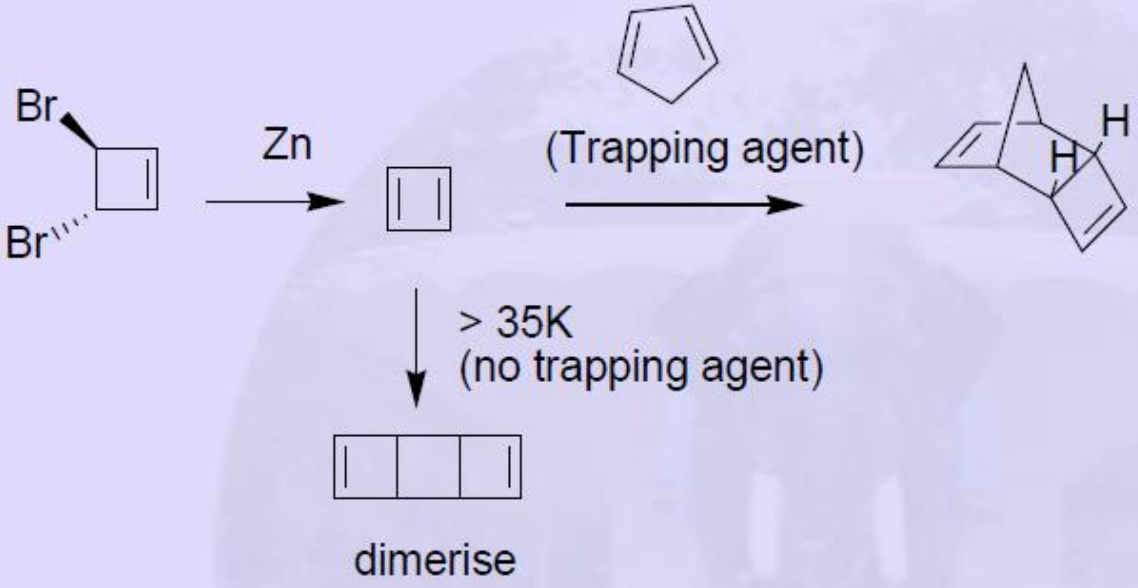
Aromatic Compounds > Non-Aromatic> Anti-Aromatic

Cyclobutadiene

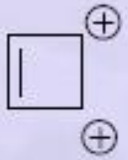


4 electrons (even number of pairs; 4n, n = 1)
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation)
Antiaromatic

Being anti-aromatic, 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.

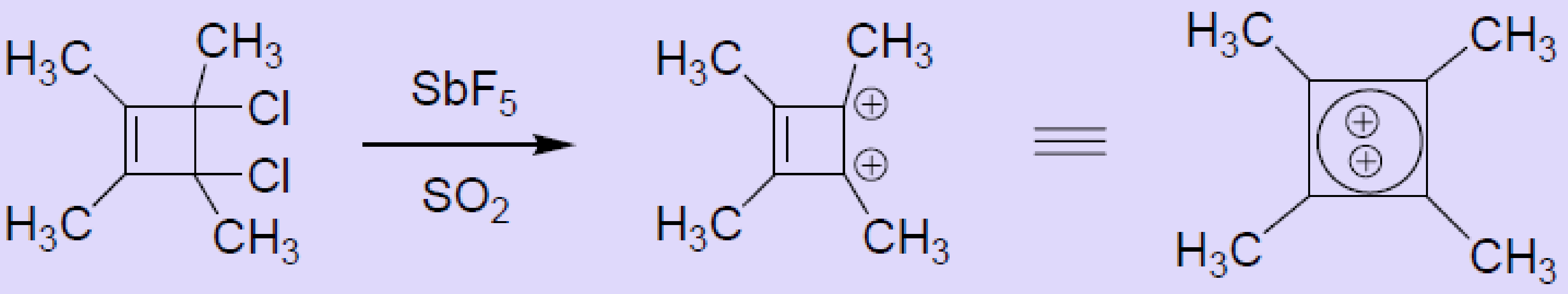


Cyclobutadienyl dication



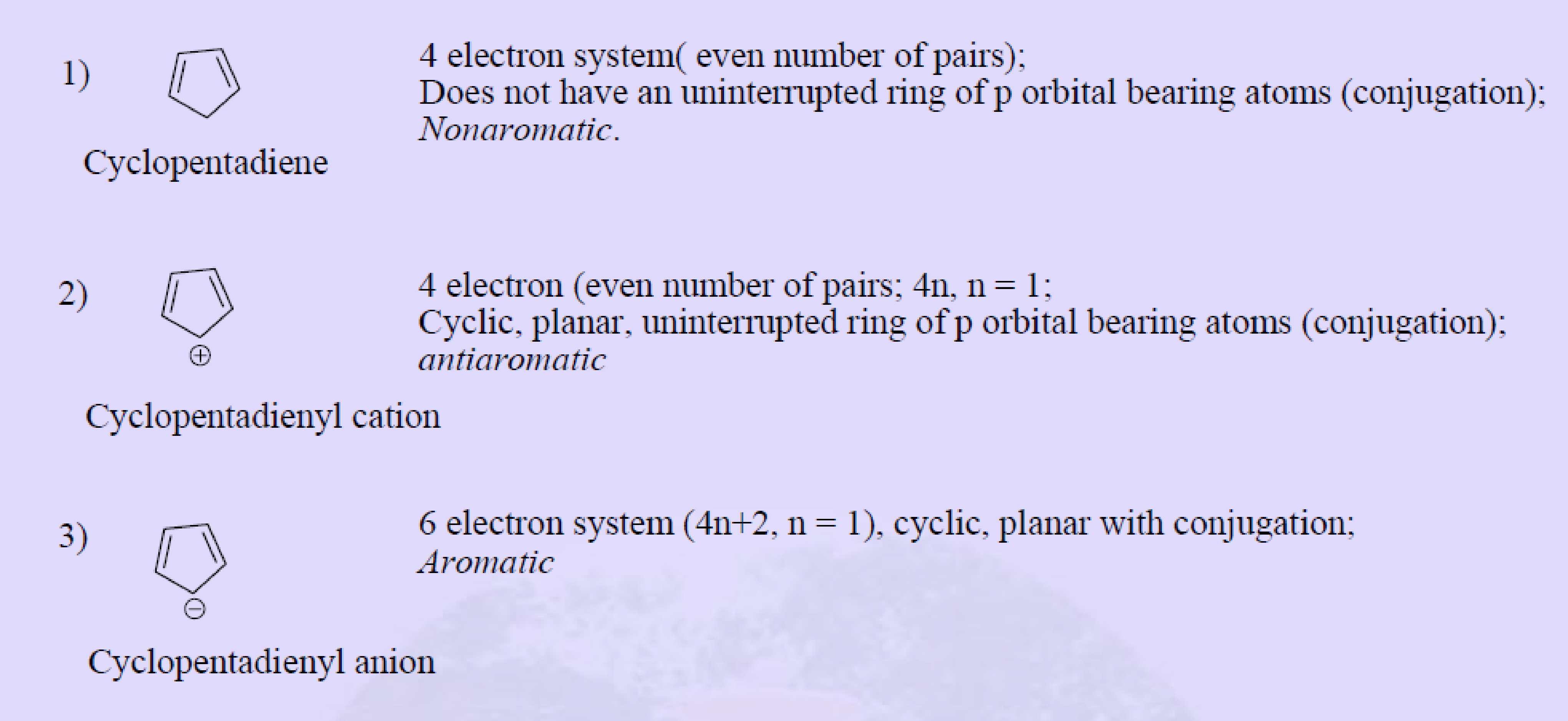
2 electrons (4n+2; n = 0); the delocalization of 2 electrons is possible through the empty p orbitals

Aromatic



Ionization of 3,4-dichloro- 1,2,3,4-tetramethylcyclobutene in SbF_5/SO_2 at -75°C leads to a dication whose formation and special stability is attributable to aromaticity.

Cyclopentadiene



1) Cyclopentadiene

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

2) Cyclopentadienyl cation

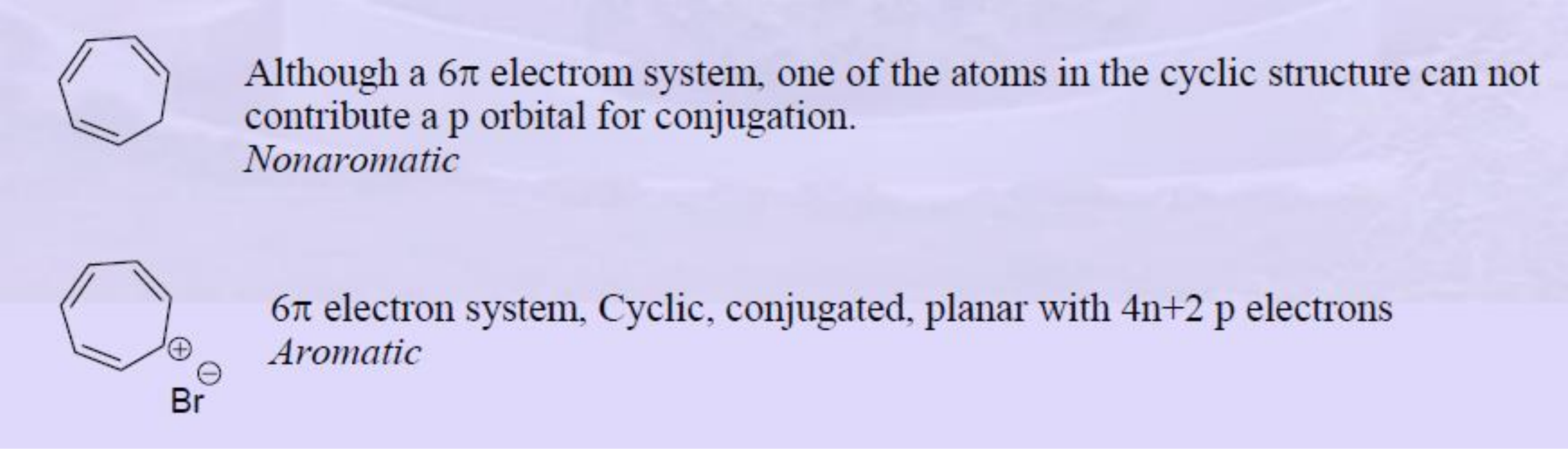
4 electron (even number of pairs; 4n, n = 1;
Cyclic, planar, uninterrupted ring of p orbital bearing atoms (conjugation);
antiaromatic

3) Cyclopentadienyl anion

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

The pKa of cyclopentadiene is 15, which is extraordinary for hydrogen bonded to a sp^3 carbon. The reason for this low pKa is its high tendency to become aromatic by releasing a proton.

7-membered rings- Cycloheptatriene

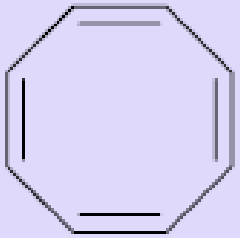


Although a 6π electrom system, one of the atoms in the cyclic structure can not contribute a p orbital for conjugation.
Nonaromatic

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

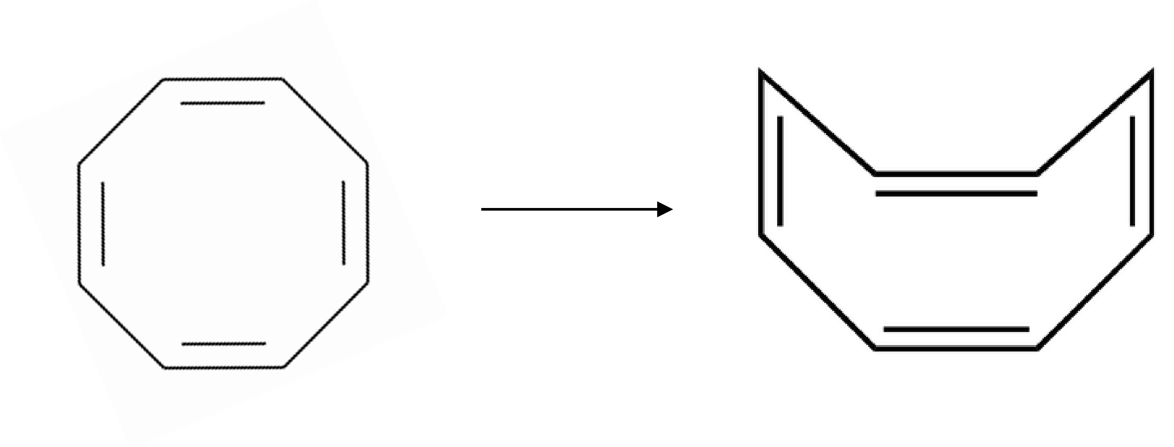


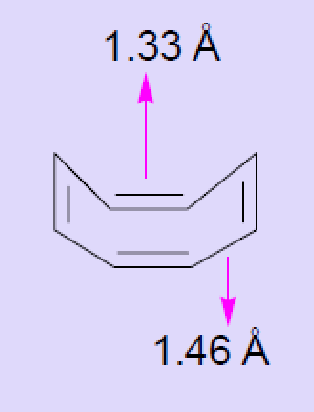
8 π electron system;

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);

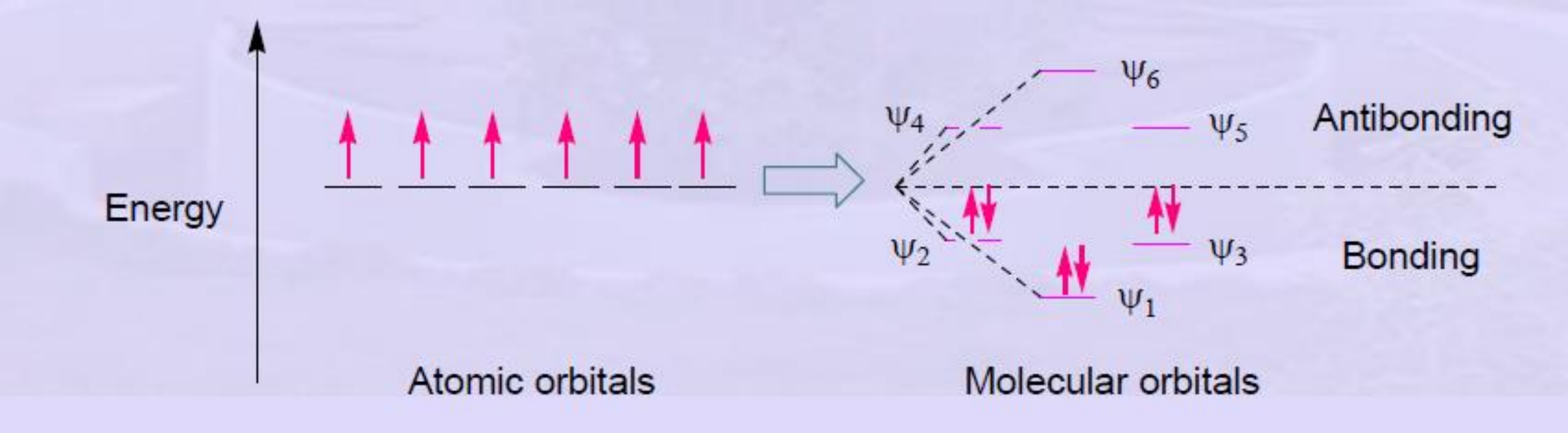
The molecule is actually boat shaped and *nonaromatic*.

(Nonaromatic form is more stable than an antiaromatic form)





Molecular orbital description of aromaticity and anti-aromaticity

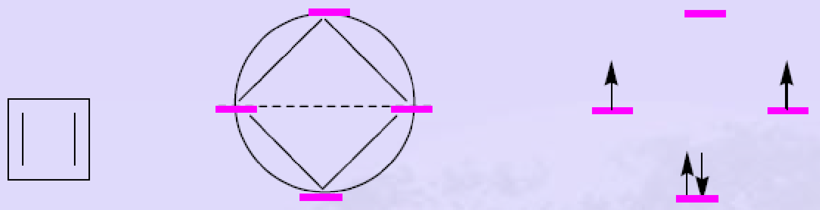


Frost Diagrams

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 Energy levels below this line indicate bonding MOs and those above are anti-bonding.

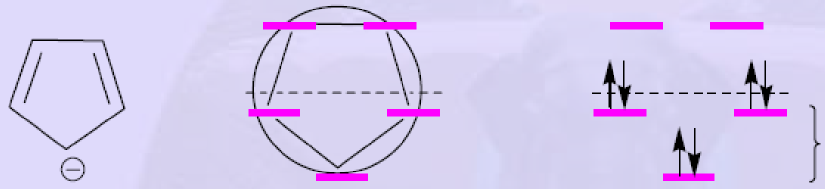


Antibonding

Nonbonding

Bonding

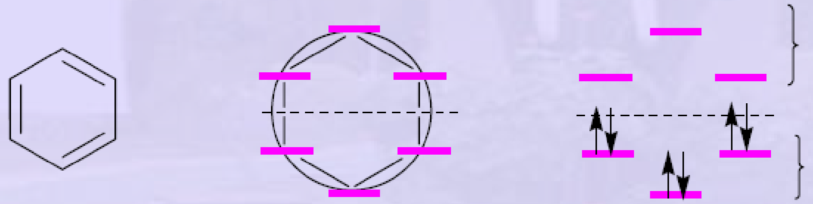
Antiaromatic



Antibonding

Bonding

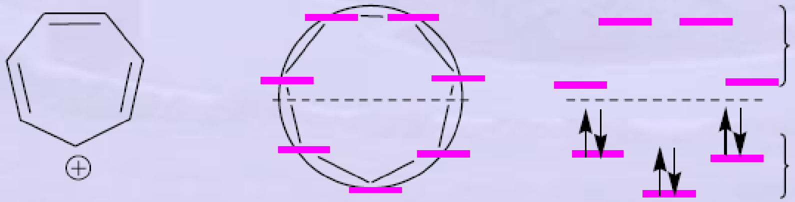
Aromatic



Antibonding

Bonding

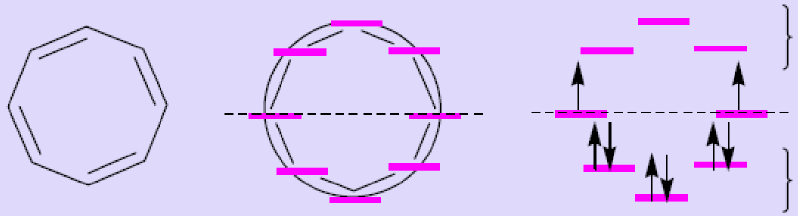
Aromatic



Antibonding

Bonding

Aromatic



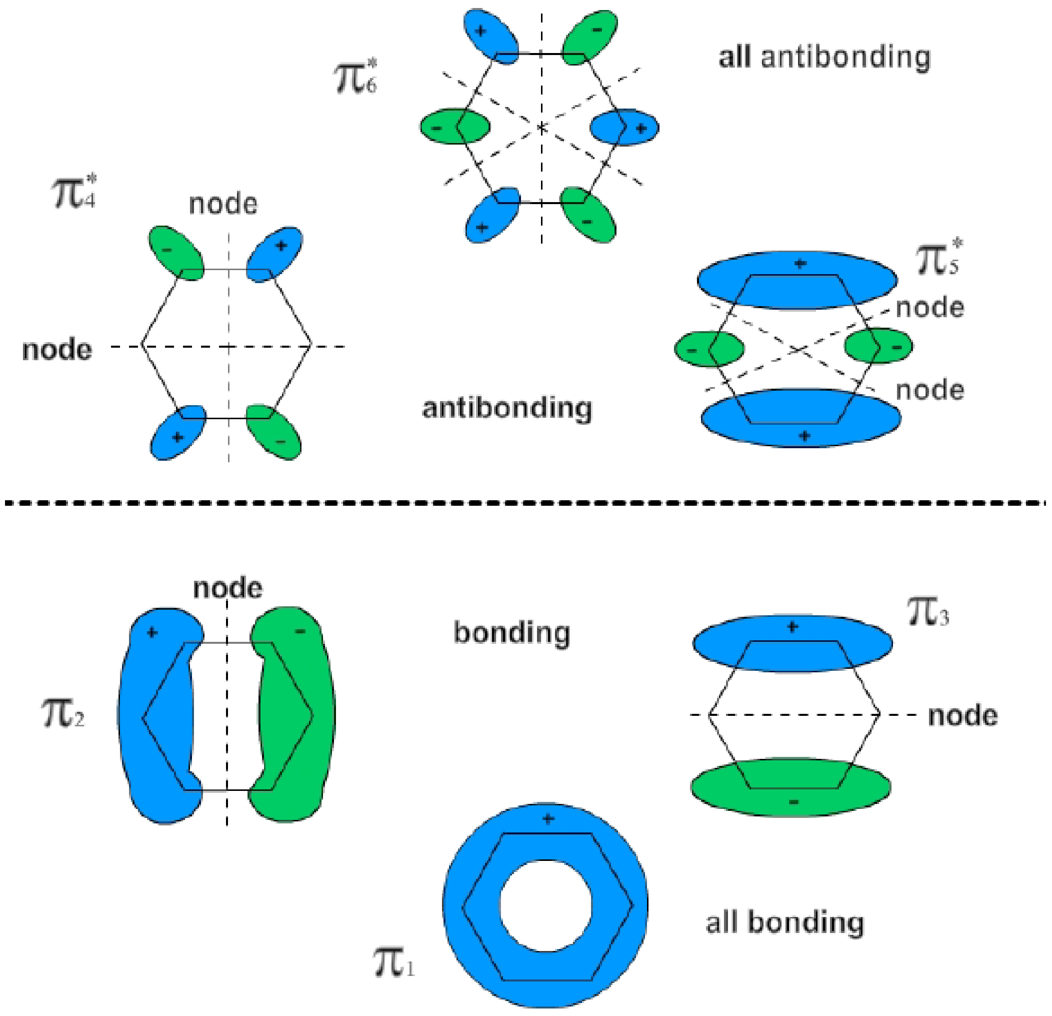
Antibonding

Nonbonding

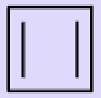
Bonding

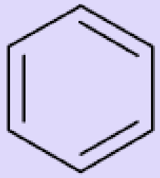
Antiaromatic

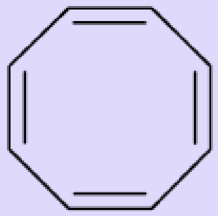
(chooses to be nonaromatic by adopting tub-shaped conformation)

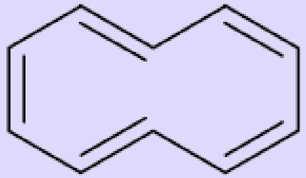


Aromaticity in higher Annulenes


[4] Annulene

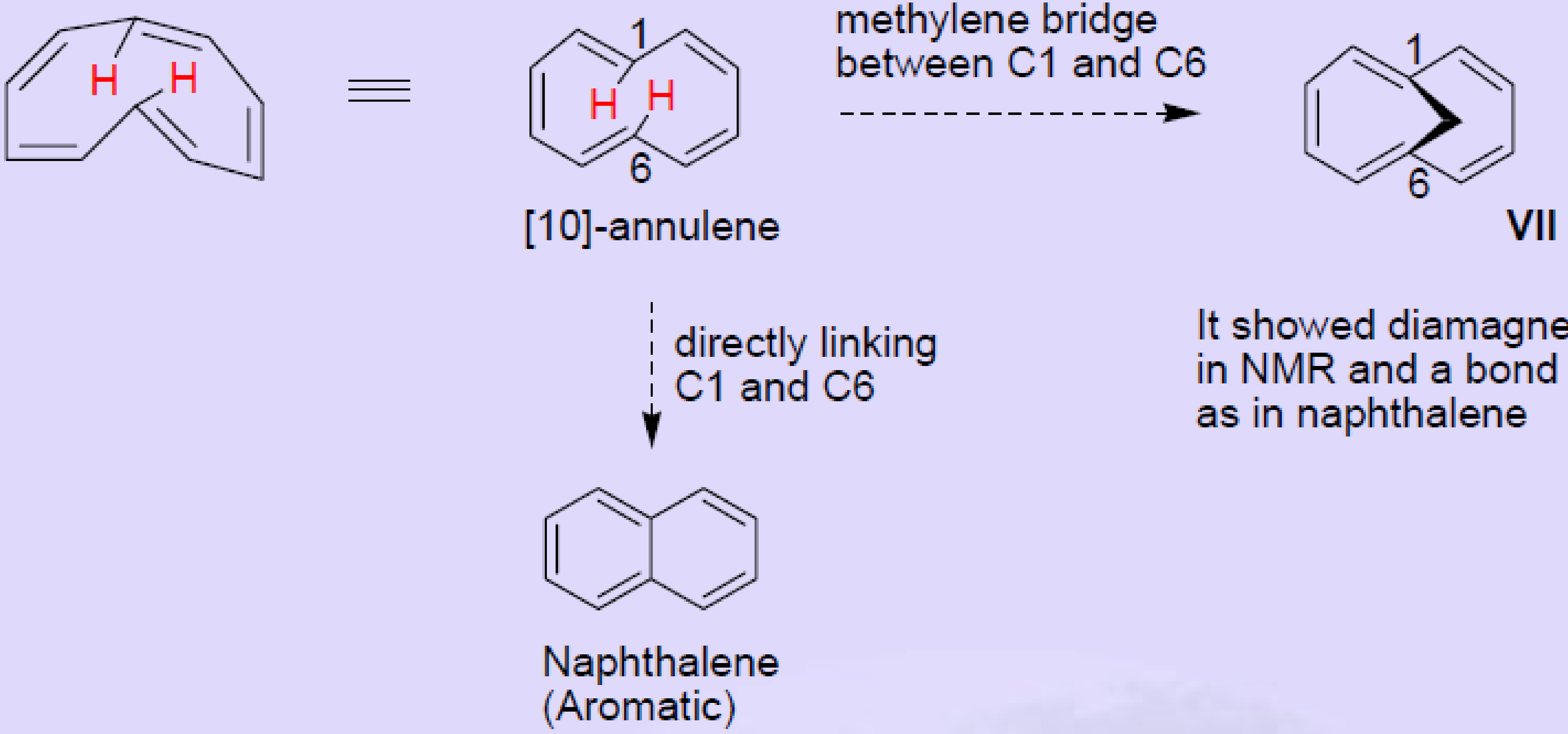

[6] Annulene


[8] Annulene


[10] Annulene

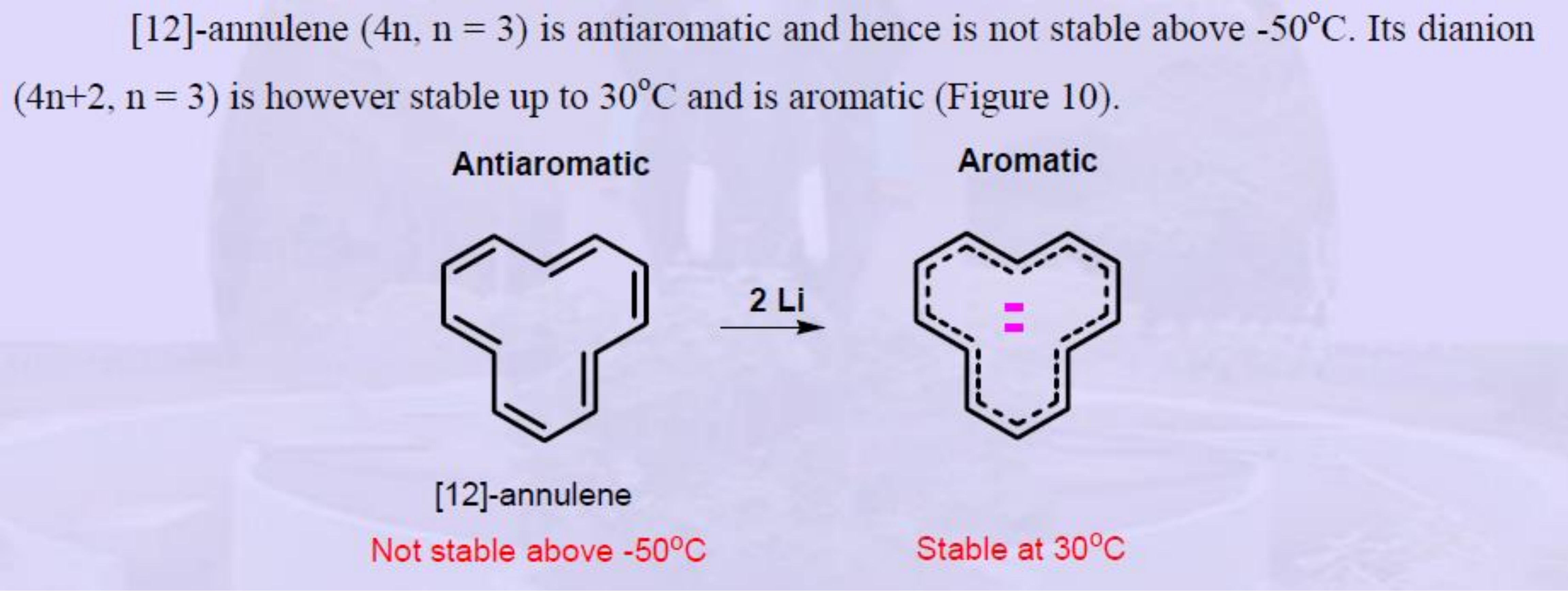
If the ring (with 4n+2 π electrons) is sufficiently large such that planarity does not cause steric or angle strains, the system would adopt that conformation, get stabilization through electron delocalization and become aromatic. Larger annulenes with 4n π electrons are not anti-aromatic because they are **flexible enough to become non-planar** and become non-aromatic.

[10]-annulene



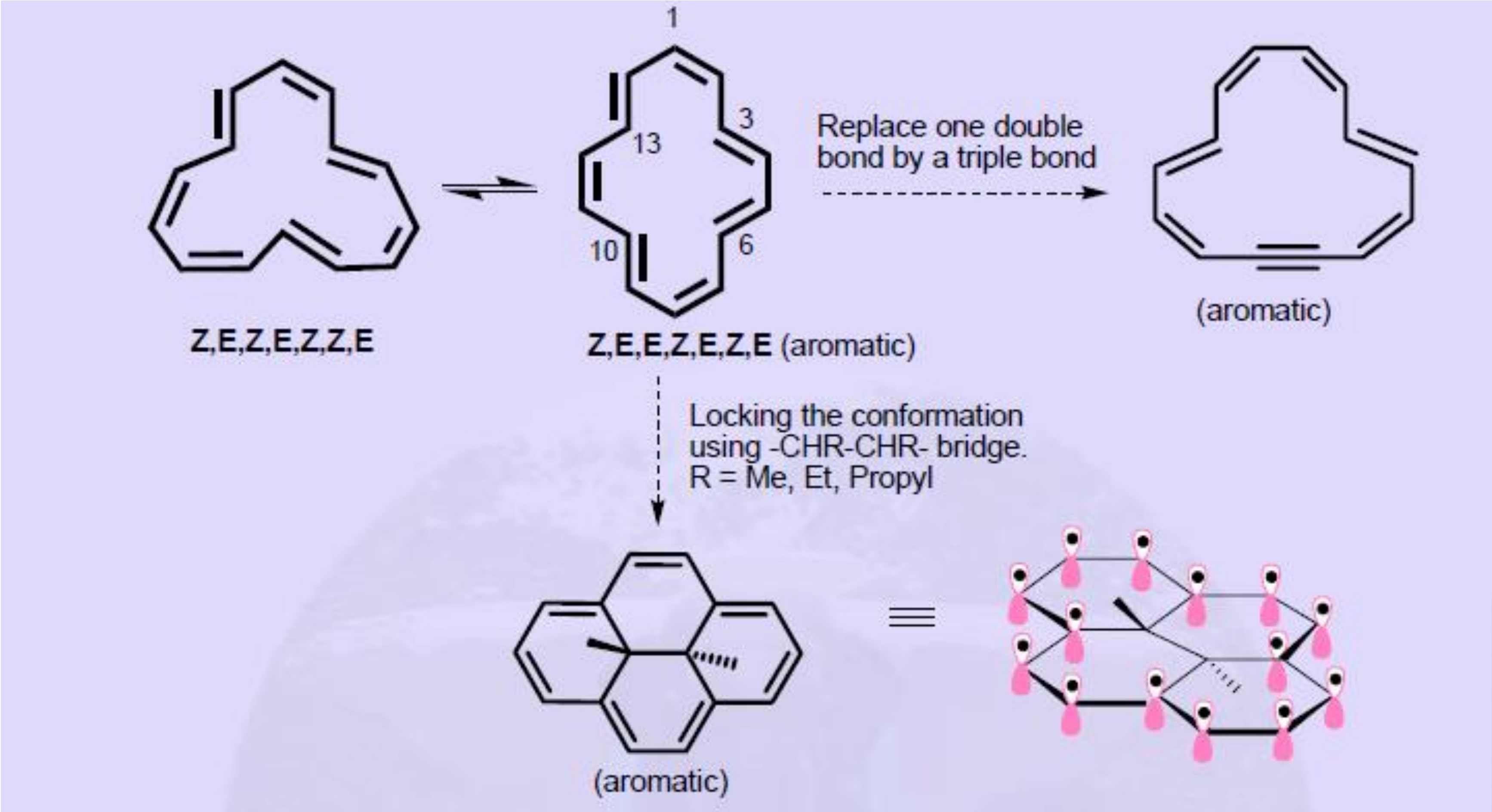
It showed diamagnetic ring current in NMR and a bond length pattern as in naphthalene

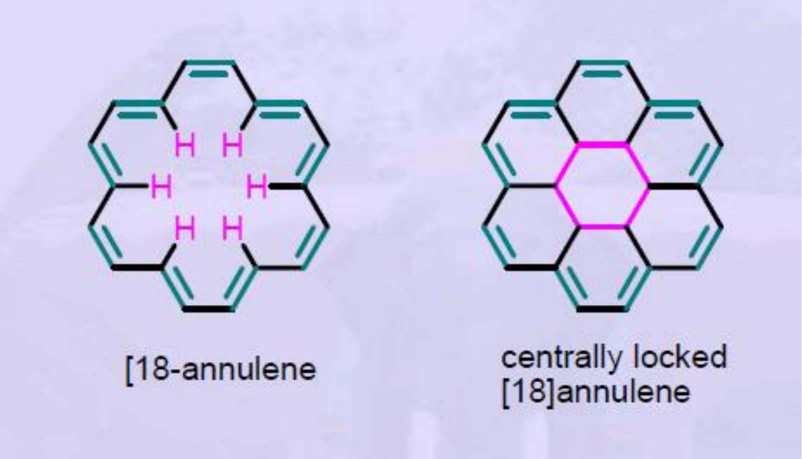
[12]-annulene



[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).

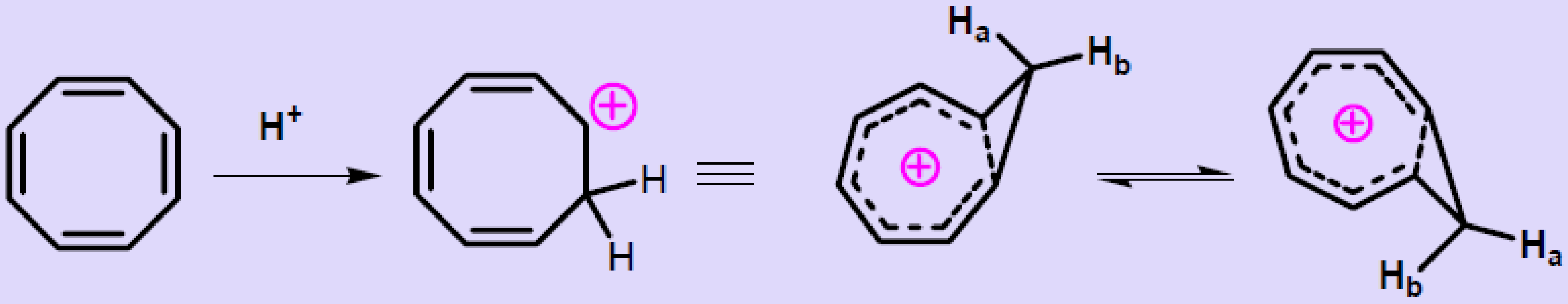
[14]-annulene


1
3
13
6
10
Z,E,Z,E,Z,Z,E
Z,E,E,Z,E,Z,E (aromatic)
Replace one double bond by a triple bond
(aromatic)
Locking the conformation using -CHR-CHR- bridge. R = Me, Et, Propyl
≡
(aromatic)

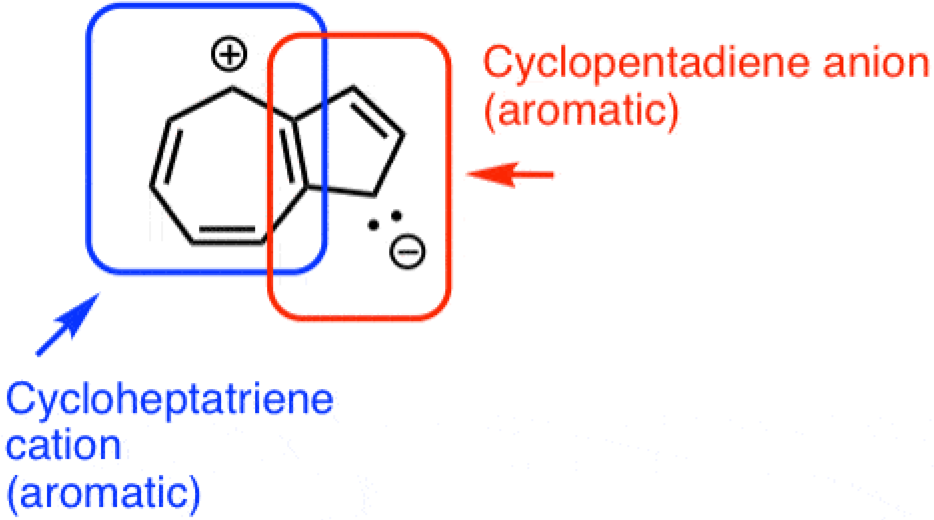

H
H
H
H
H
H
[18-annulene
centrally locked [18]annulene

Homoaromaticity

If a stabilized cyclic conjugated system (4n+2 es) 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.

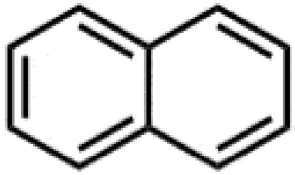


Important resonance form of azulene



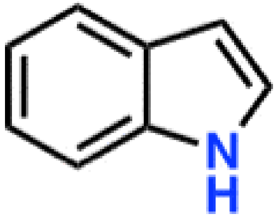
Aromaticity

No, it's not! There are many other molecules which possess this collection of traits, which we call "aromaticity". Some examples:

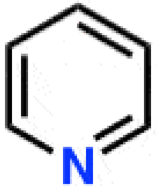


Naphthalene

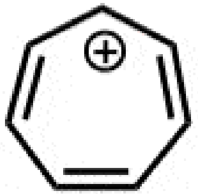
Furan



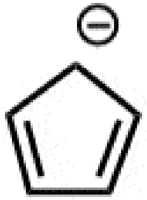
Indole



Pyridine

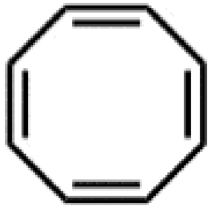


Tropylium ion



Cyclopentadienyl anion

Counter-example



Cyclooctatetraene (*not* aromatic)