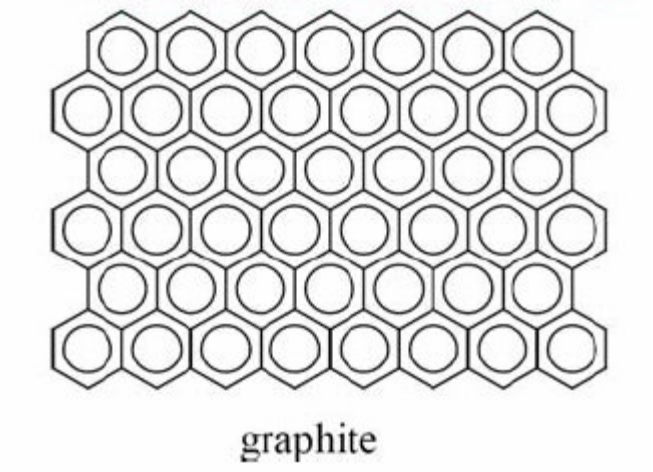
Química Orgânica I

Profa. Dra. Alceni Augusta Werle
Profa. Dra. Tania Márcia do Sacramento Melo

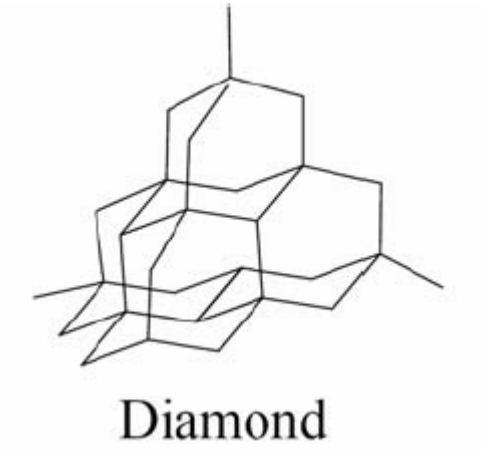
Aromaticidade

Aula nº 9

Qual o nome dos seguintes compostos? Qual a diferença entre eles?



graphite



Diamond

Tipos de compostos organicos

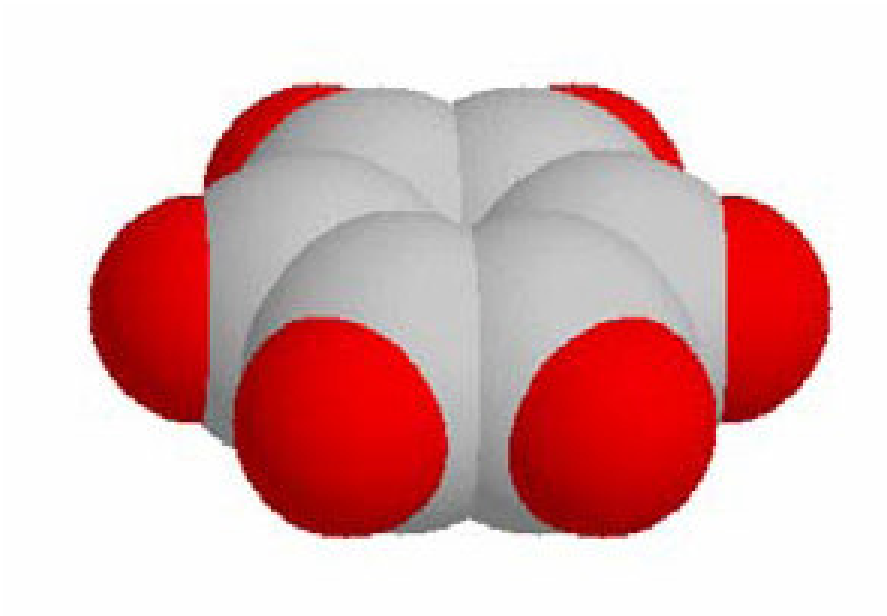
- **Alifaticos**

  Alcanos, alquenos, cetonas.....

- **Aromaticos**

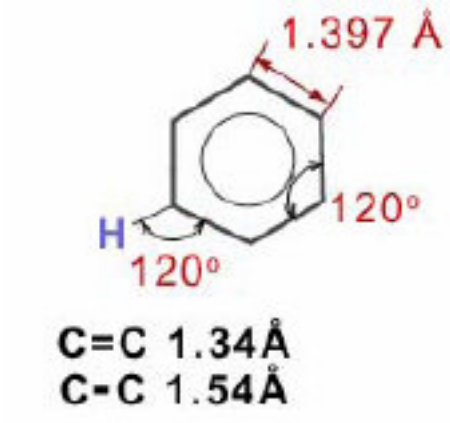
  Benzeno, naltaleno, piridina.....

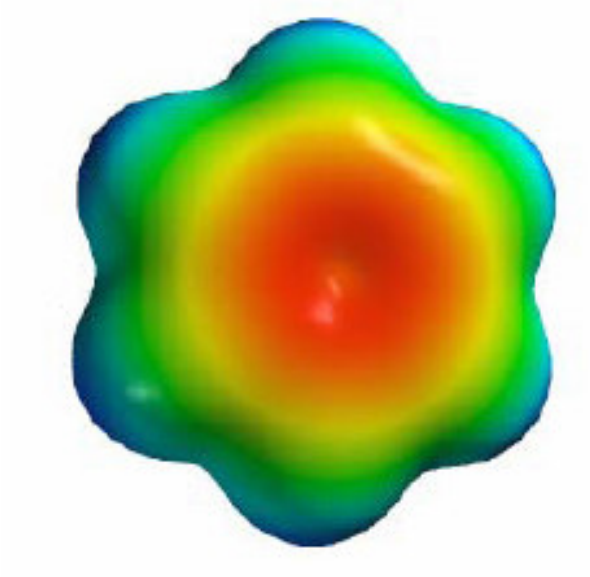
1- Compostos aromaticos e anti-aromaticos



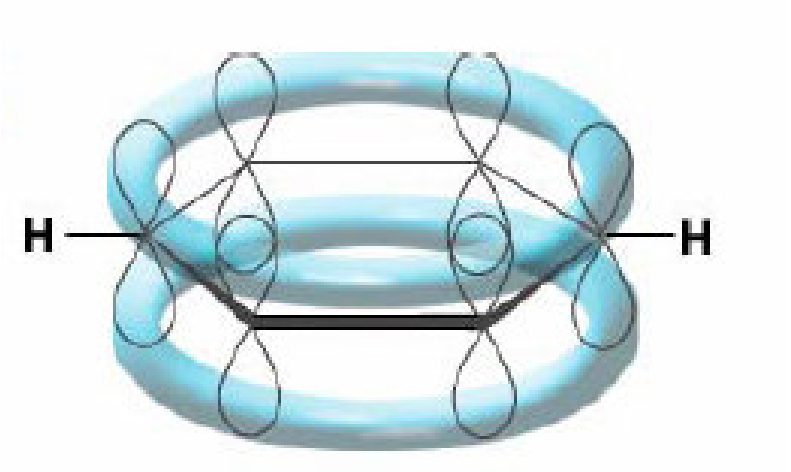
1.1- A estrutura do benzeno e aromaticidade

- Estrutura com os mesmos comprimentos de ligacao.





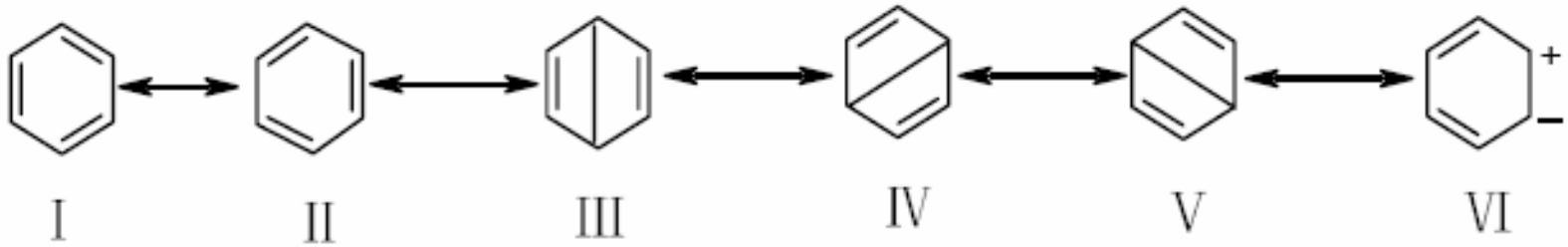
Como explicar o mapa de potencial eletrostatico?



Cada carbono sp^2 possui um orbital p perpendicular ao plano das ligacoes σ, fazendo *overlaps* por todo o anel

Esta foi a única propsota para o benzeno?

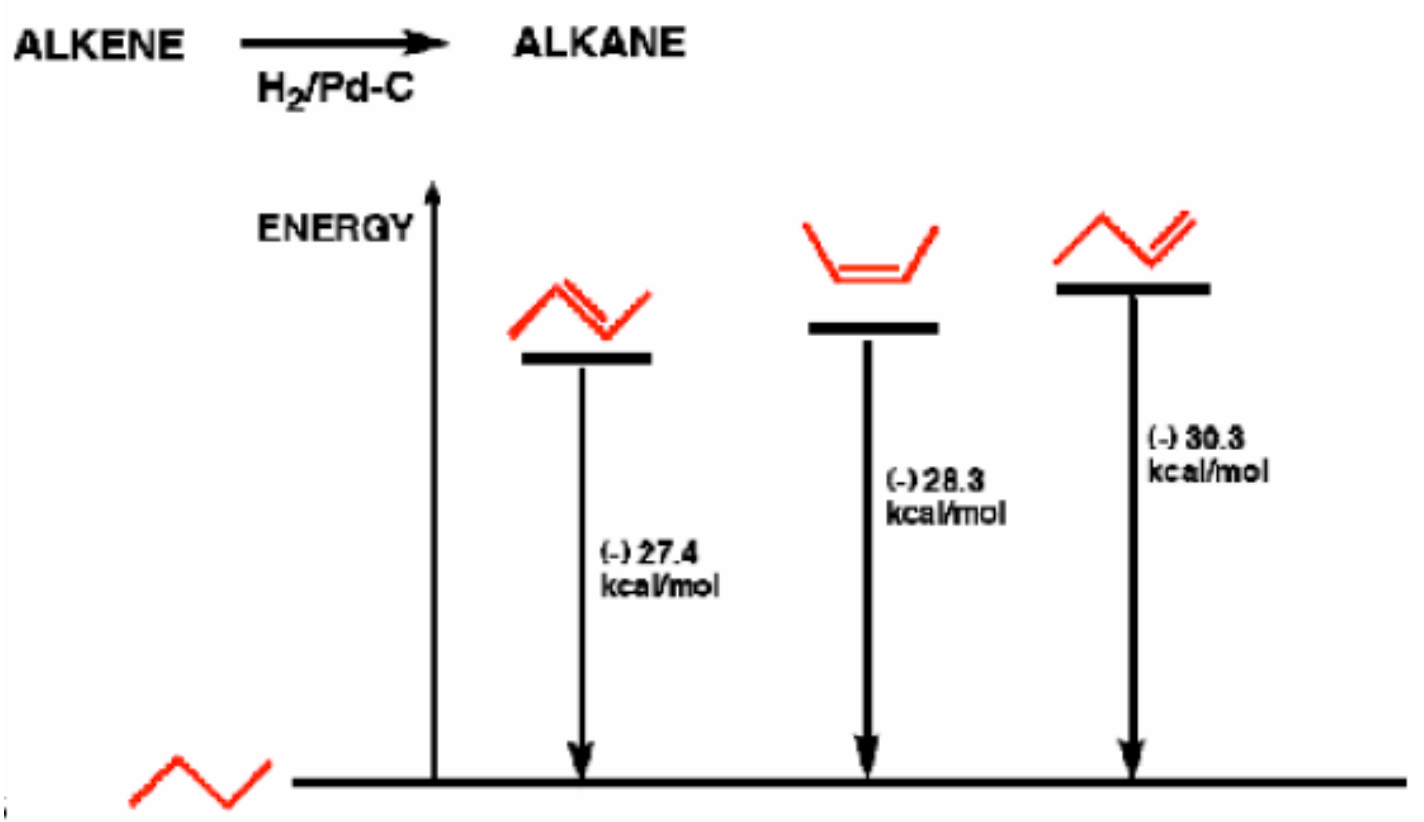
Estruturas de ressonancia teoricamente possiveis



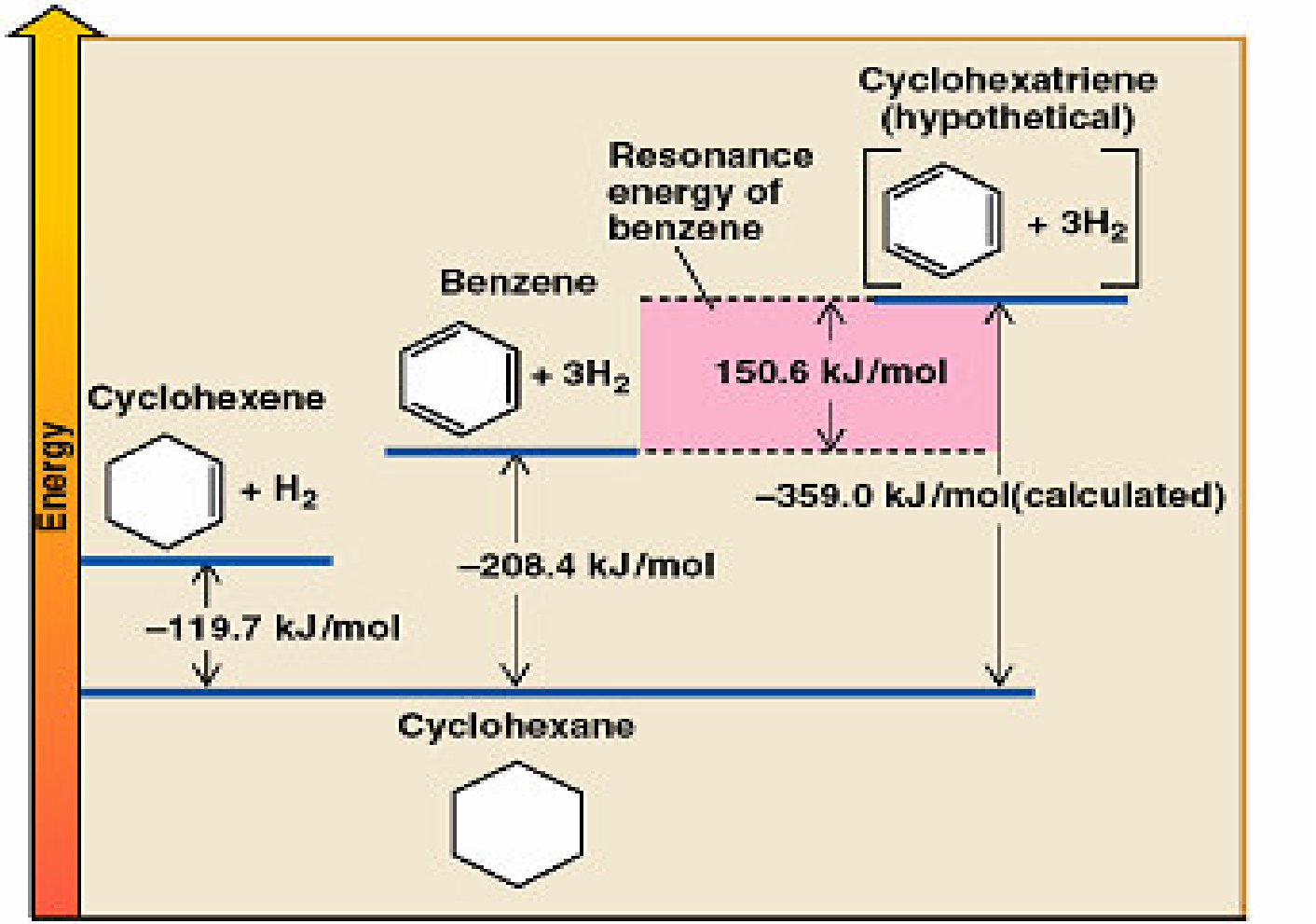
Todas são reais?

Comprovacoes do comportamento diferenciado do benzeno

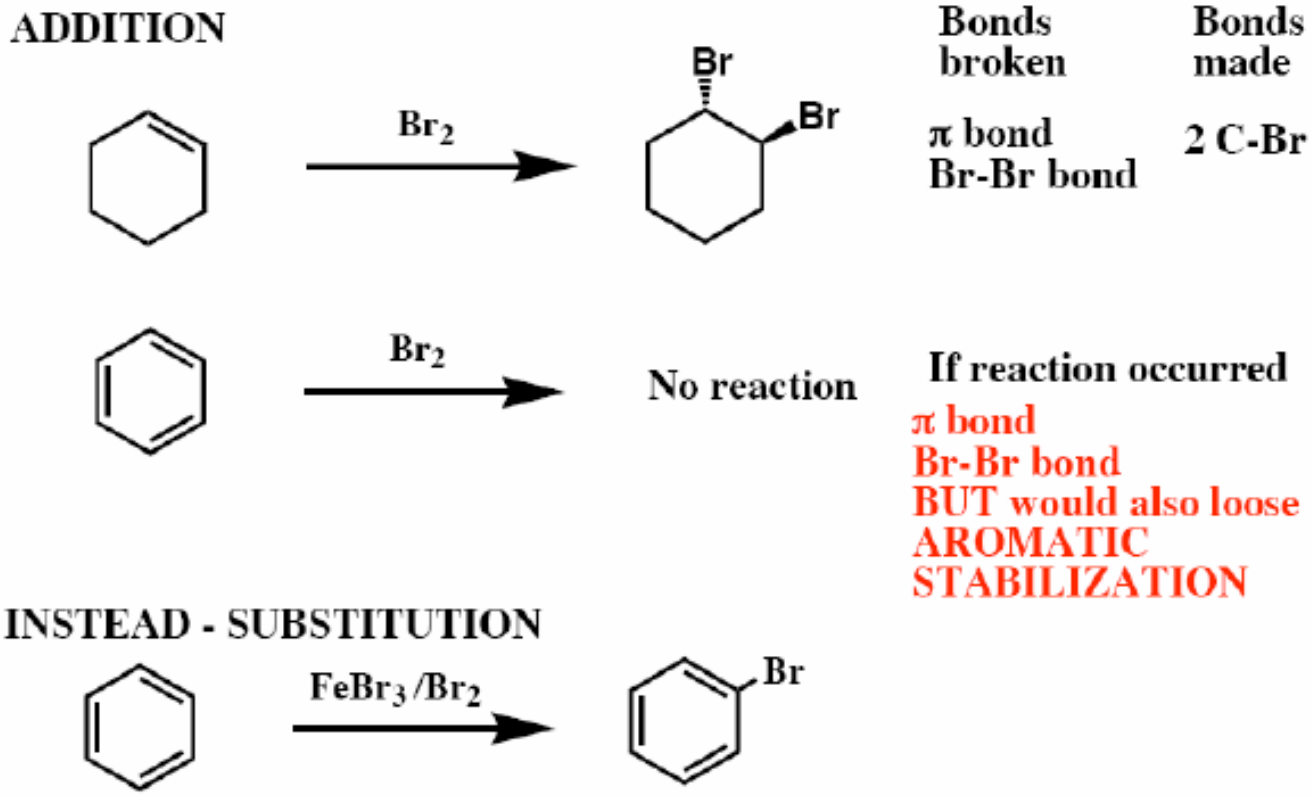
- Calor de hidrogenacao (ΔH^0) revela estabilidade



Calor de hidrogenacao para o benzeno - excepcional energia de ressonancia



2- Efeitos da estabilizacao nas reações do benzeno



Conclusao: o benzeno não e um trieno e sim um aromatico

3- Definicao de aromaticidade

- **Aromaticidade** e uma propriedade associada a com uma excepcional estabilidade que ocorre em certos sistemas π.
- Compostos aromaticos: aqueles que apresentam **aromaticidade**.

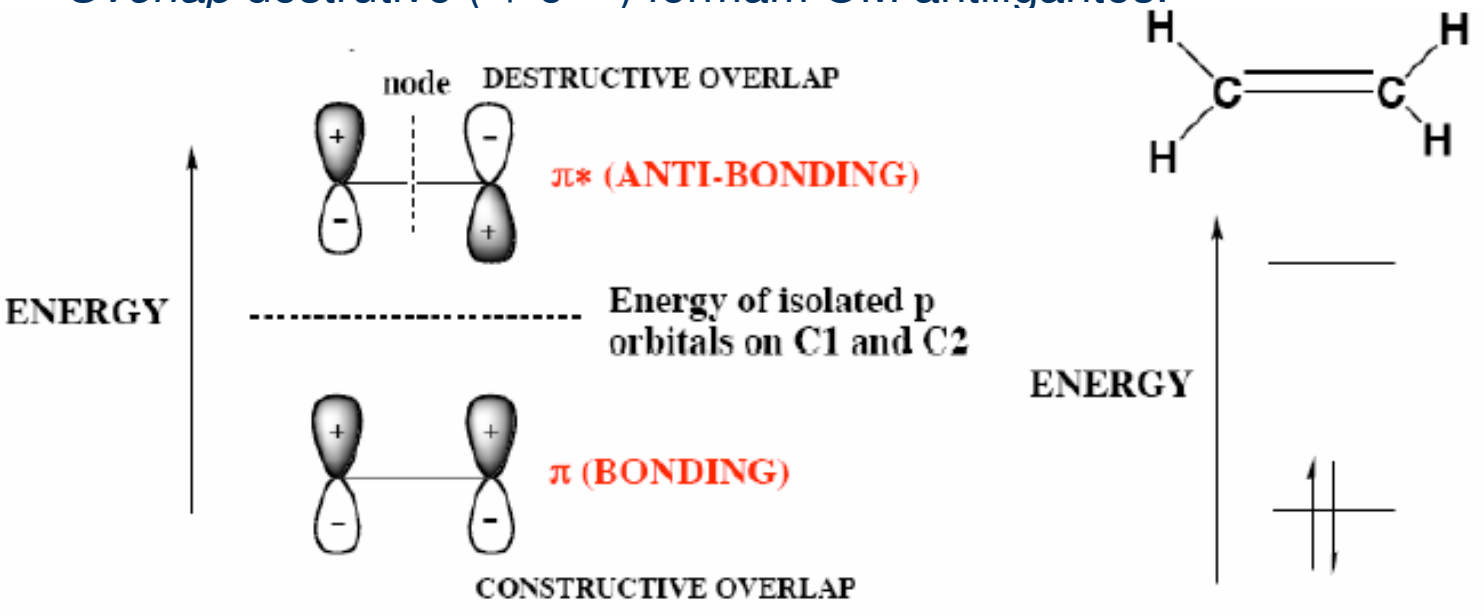
4- Criterio de aromaticidade a anti-aromaticidade

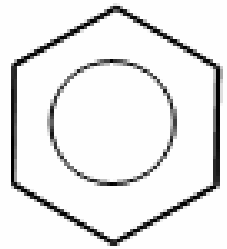
- Anulenos: hidrocarbonetos ciclicos conjugados.

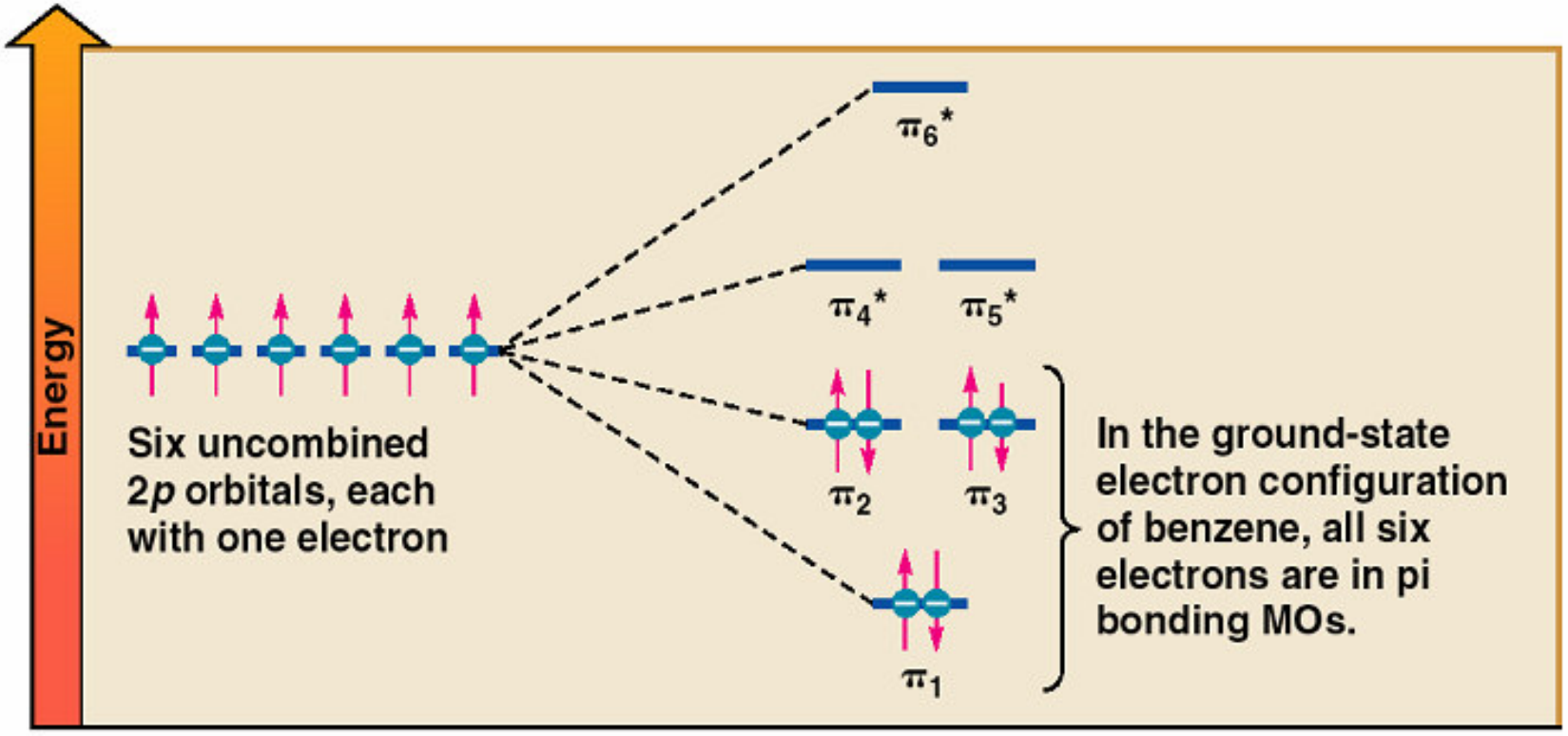
- Inicialmente, todos os anulenos foram propostos como aromaticos, entretanto o ciclobutadieno dimeriza mesmo antes do seu isolamento e o cicloctatetraeno adiciona Br_2 rapidamente.

5- Orbitais moleculares (OM)

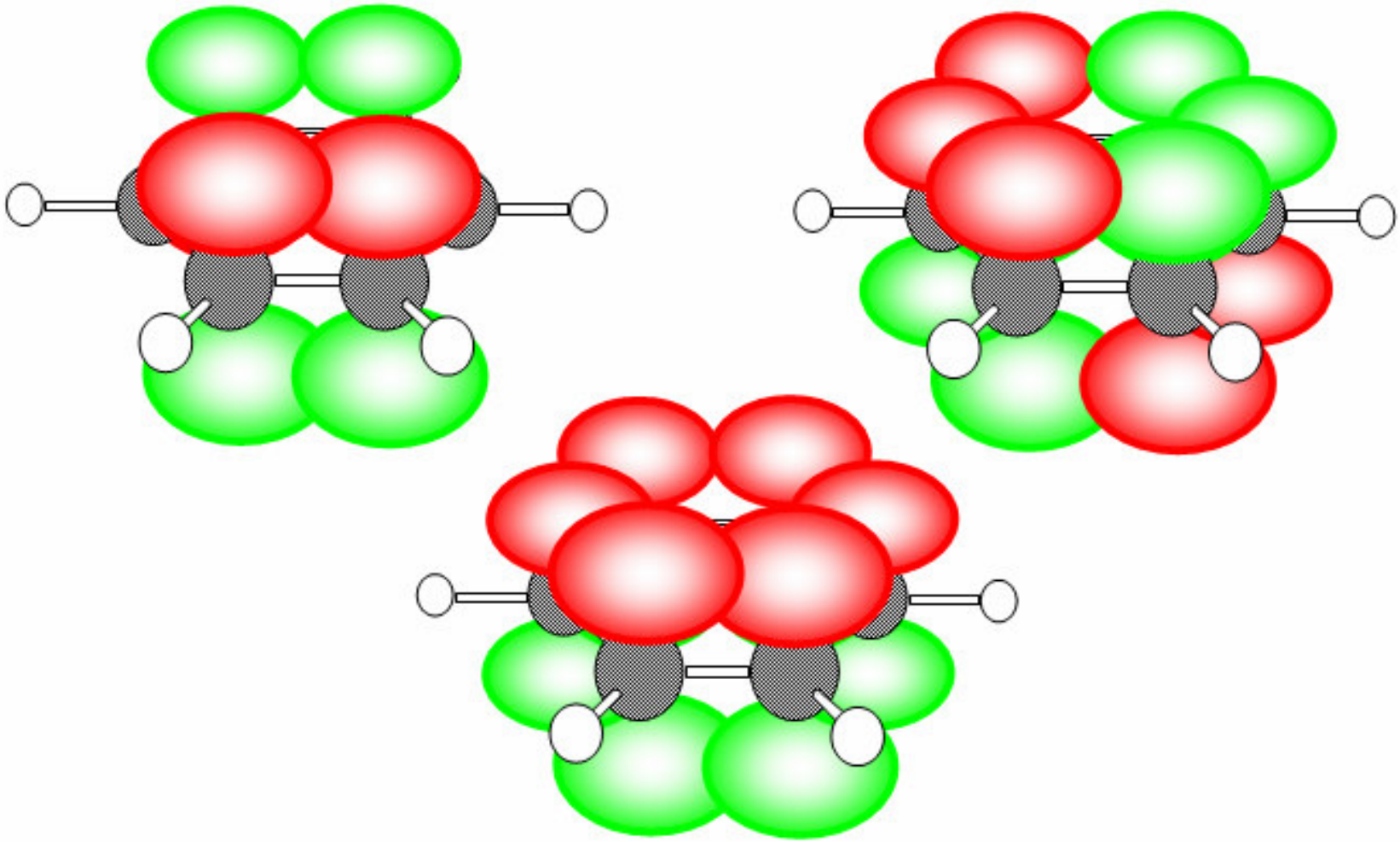
- OM π resultam do *overlap* de orbitais p.
- Orbitais p são bilobulares, fase (+) e (-), não significa carga e sim funcao.
- *Overlap* construtivo (+ e + ou - e -) formam OM ligantes.
- *Overlap* destrutivo (+ e –) formam OM antiligantes.

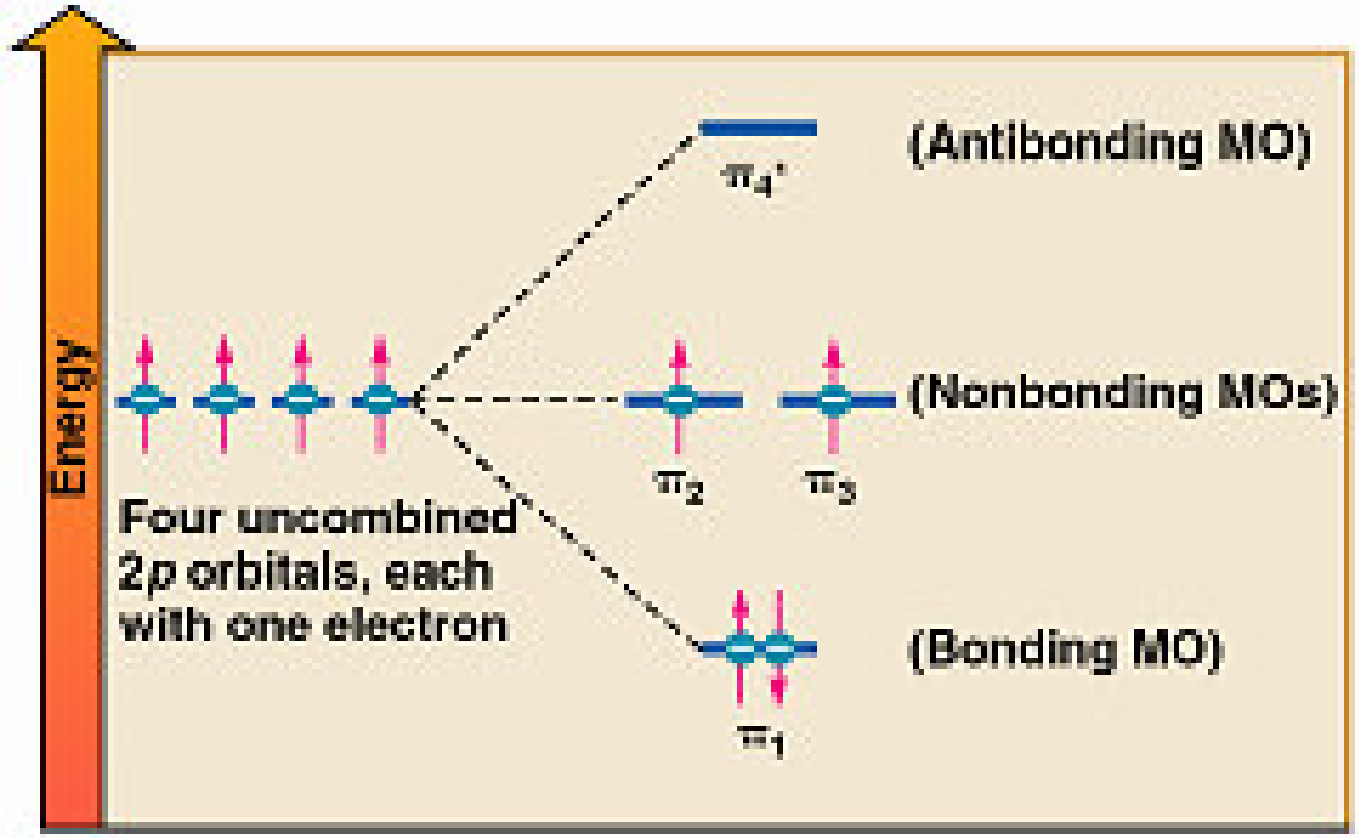


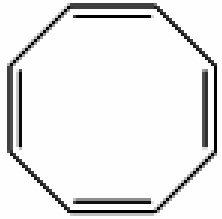


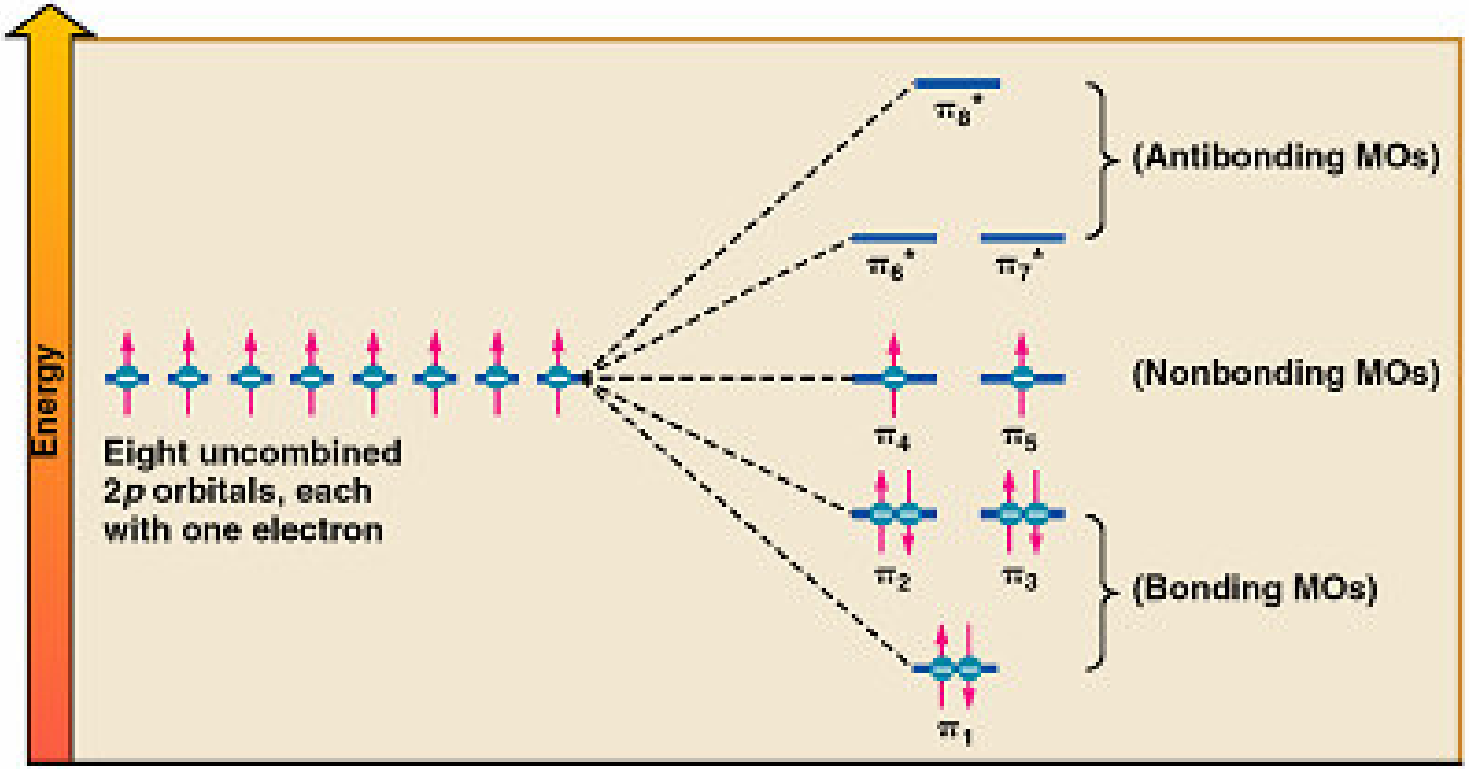

Energy
Six uncombined 2p orbitals, each with one electron
π6*
π4*
π5*
π2
π3
π1
In the ground-state electron configuration of benzene, all six electrons are in pi bonding MOs.

Orbitais moleculares ligantes do benzeno

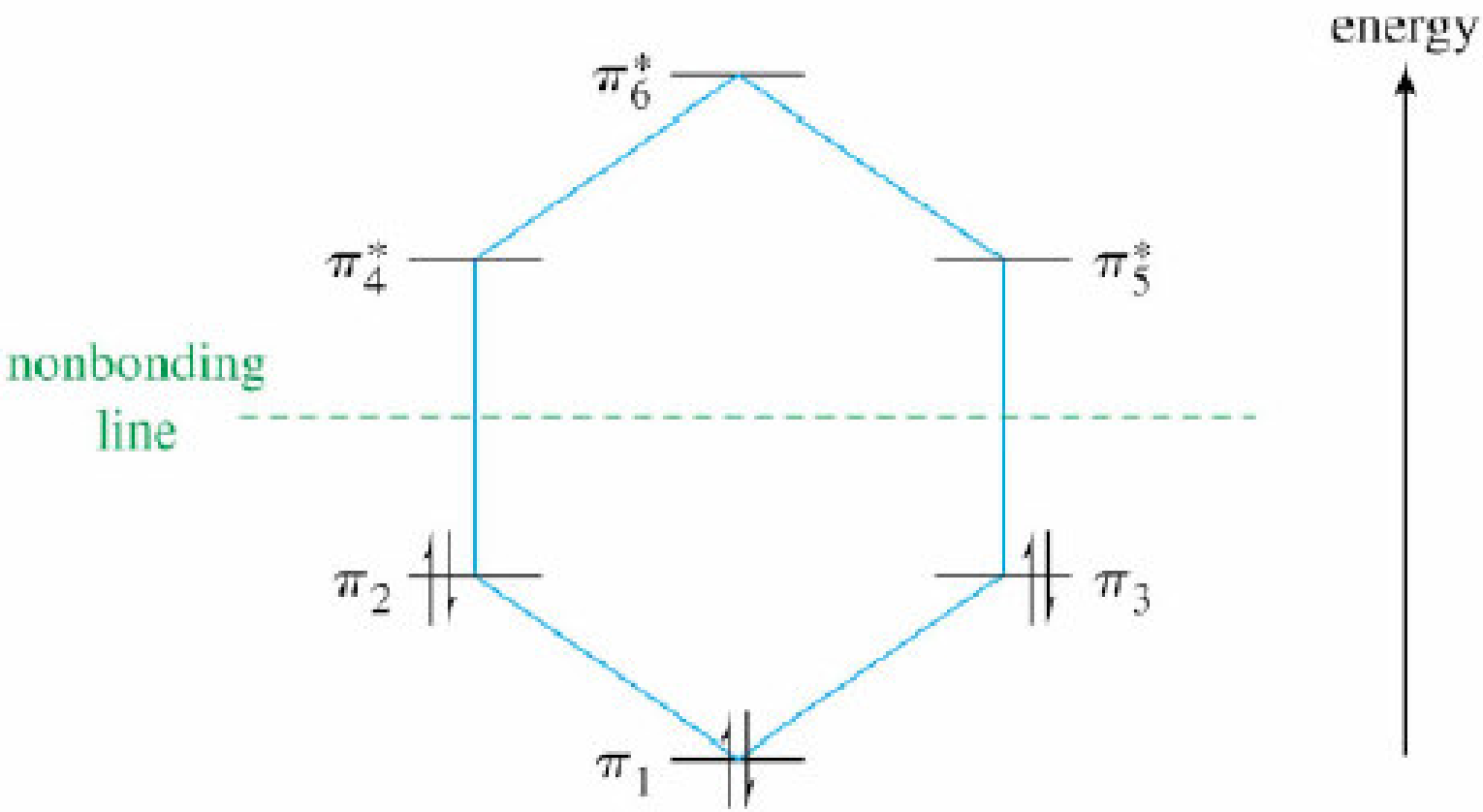



Energy
(Antibonding MO)
π_4^*
(Nonbonding MOs)
π_2
π_3
Four uncombined
2p orbitals, each
with one electron
(Bonding MO)
π_1

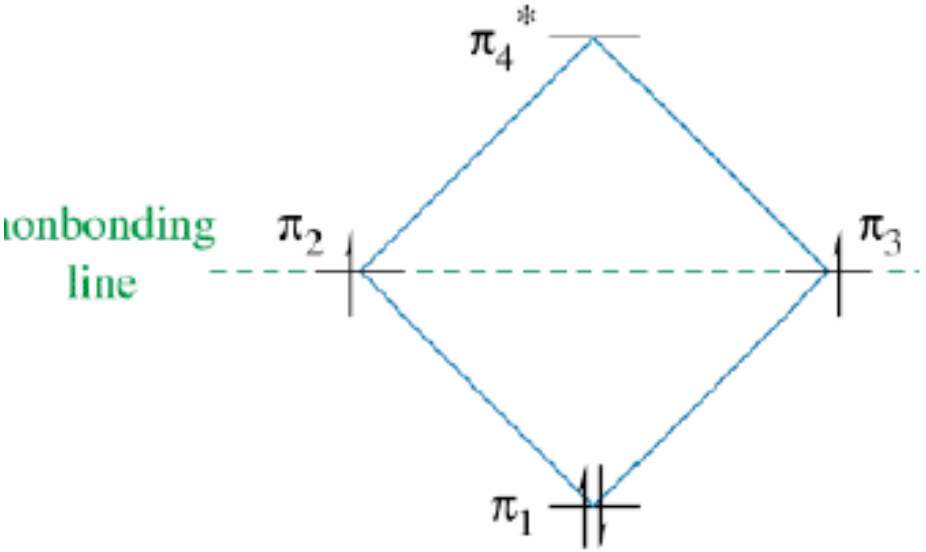


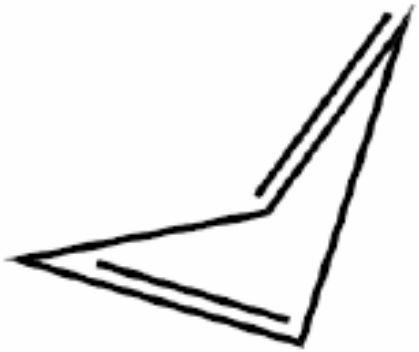

Energy
Eight uncombined
2p orbitals, each
with one electron
π8*
π6*
π7*
(Antibonding MOs)
π4
π5
(Nonbonding MOs)
π2
π3
(Bonding MOs)
π1

6- Regra do OM para o benzeno



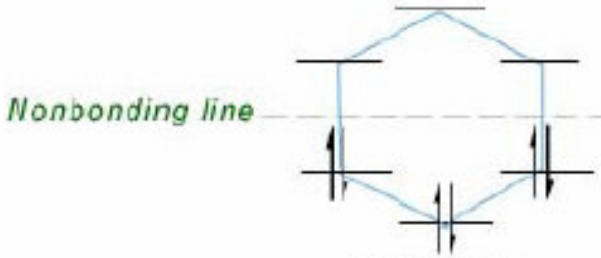
7- Regra do OM para o ciclobutadieno



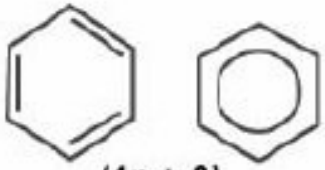


Cyclobutadiene is ANTIAROMATIC

Aromatic



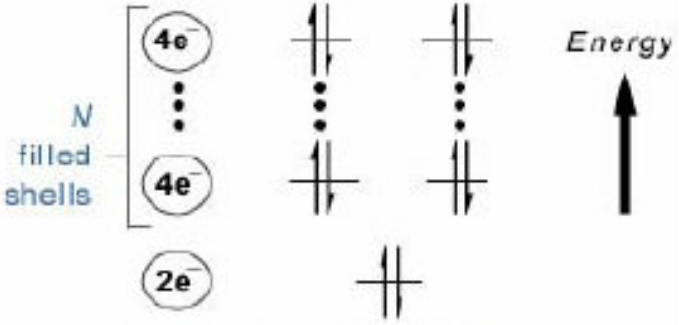
Benzene



(4n + 2)

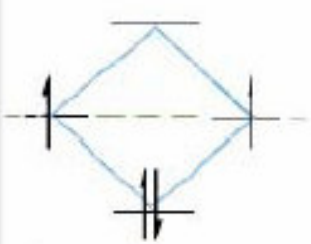
All bonds same length

(vacant orbitals not shown)

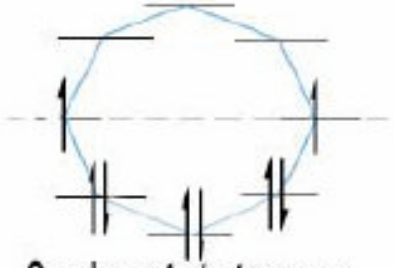


Aromatic: (4*N* +2) electrons

Anti-aromatic



Cyclobutadiene

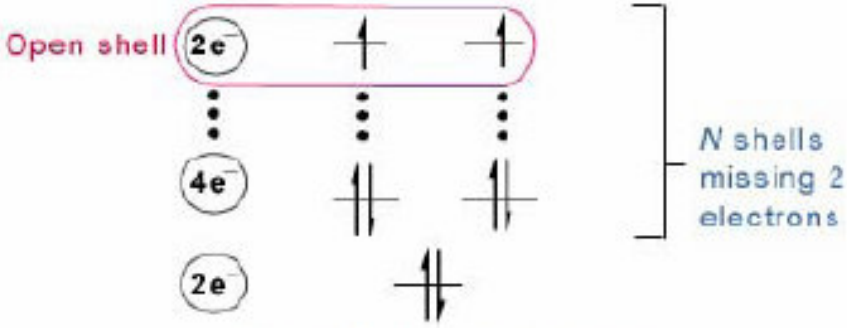


Cyclooctatetraene

(4n)

Combination of single and double bonds

(vacant orbitals not shown)



Anti-aromatic: 4*N* electrons

8- Aromaticidade segundo a Regra de Huckel

- O fisico- quimico alemao Erich Huckel , em 1930, atraves de calculos de OM constatou que moleculas ciclicas planares com 2,6,10,14,18,22.... e^- π conjugados apresentavam aromaticidade.

Hückel Regel:

Alle cyclischen konjugiert-ungesättigten Verbindungen mit

Planaren π-System und (4n + 2) π-Elektronen (n = 0, 1, 2, 3, …)

Haben aromatsichen Charakter

- Esta regra foi constatada para moleculas mono-ciclicas planares, onde os OM ligantes estao completos e os OM não ligantes e anti-ligantes não possuem eletrons .

Regra de Huckel

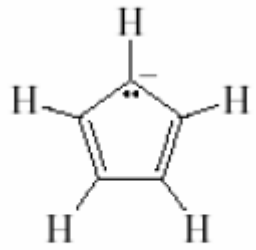
- **Polienos monociclicos planares conjugados**

$$(4\,n + 2)\,\pi \text{ electrons}$$

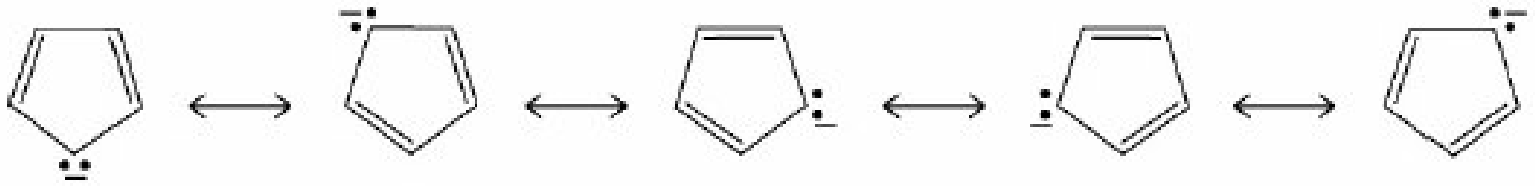
n = 0,1, 2, 3 ....

são aromaticos

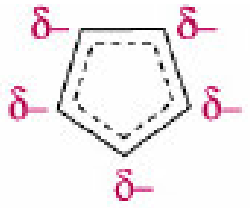
9- Aromaticidade em outra moleculas



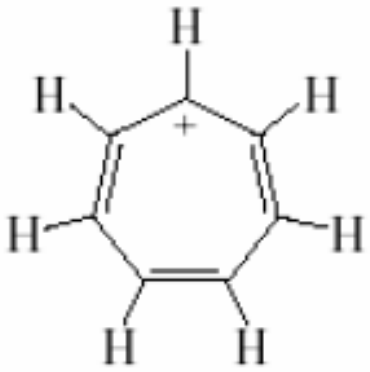
Cyclopentadienide anion
(six π electrons)



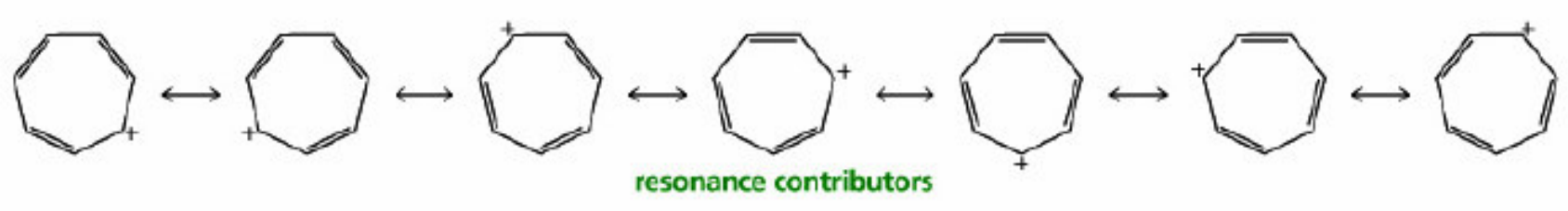
resonance contributors

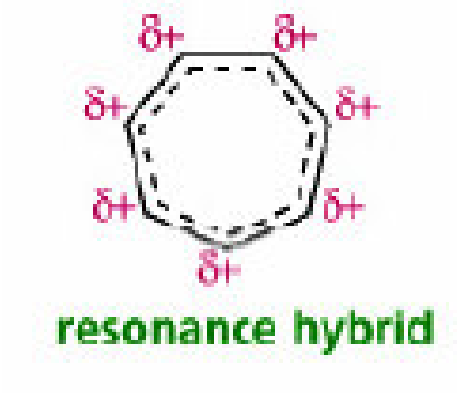


resonance hybrid



Cycloheptatrienyl cation

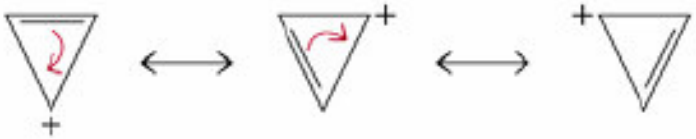




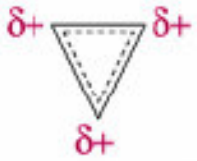
cyclopropene

cyclopropenyl cation

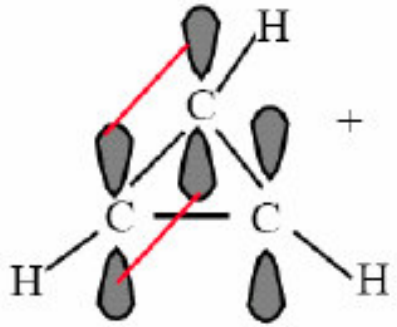
cyclopropenyl anion



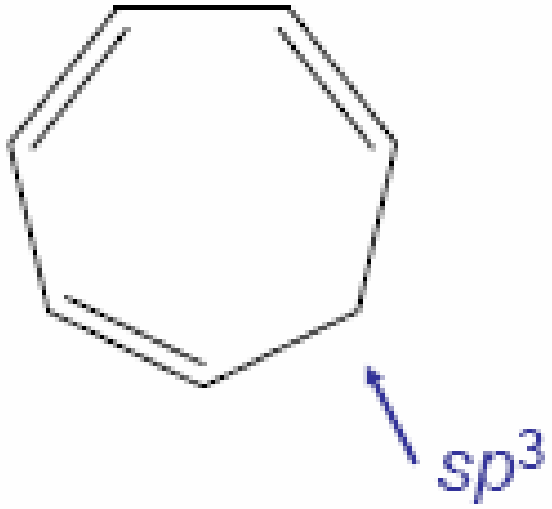
resonance contributors for the cyclopropenyl cation



resonance hybrid

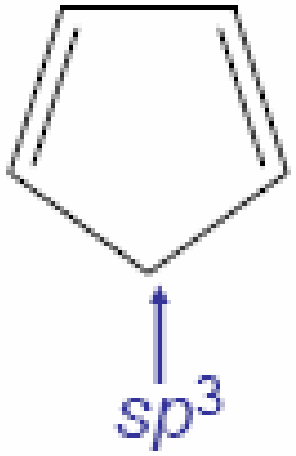


2 π electrons



cycloheptatriene

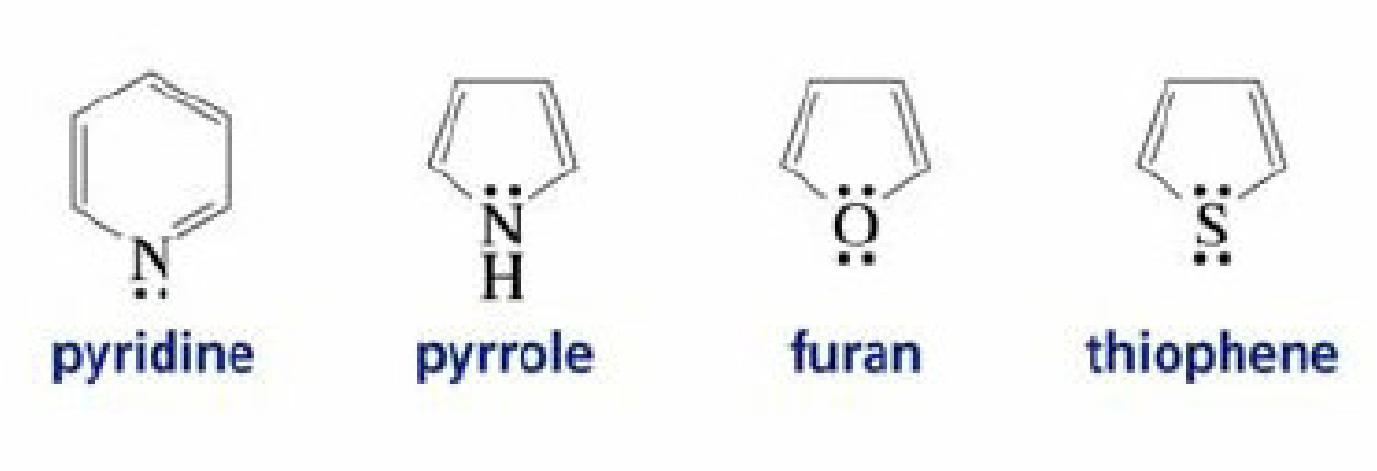
interrupted π cloud
not aromatic



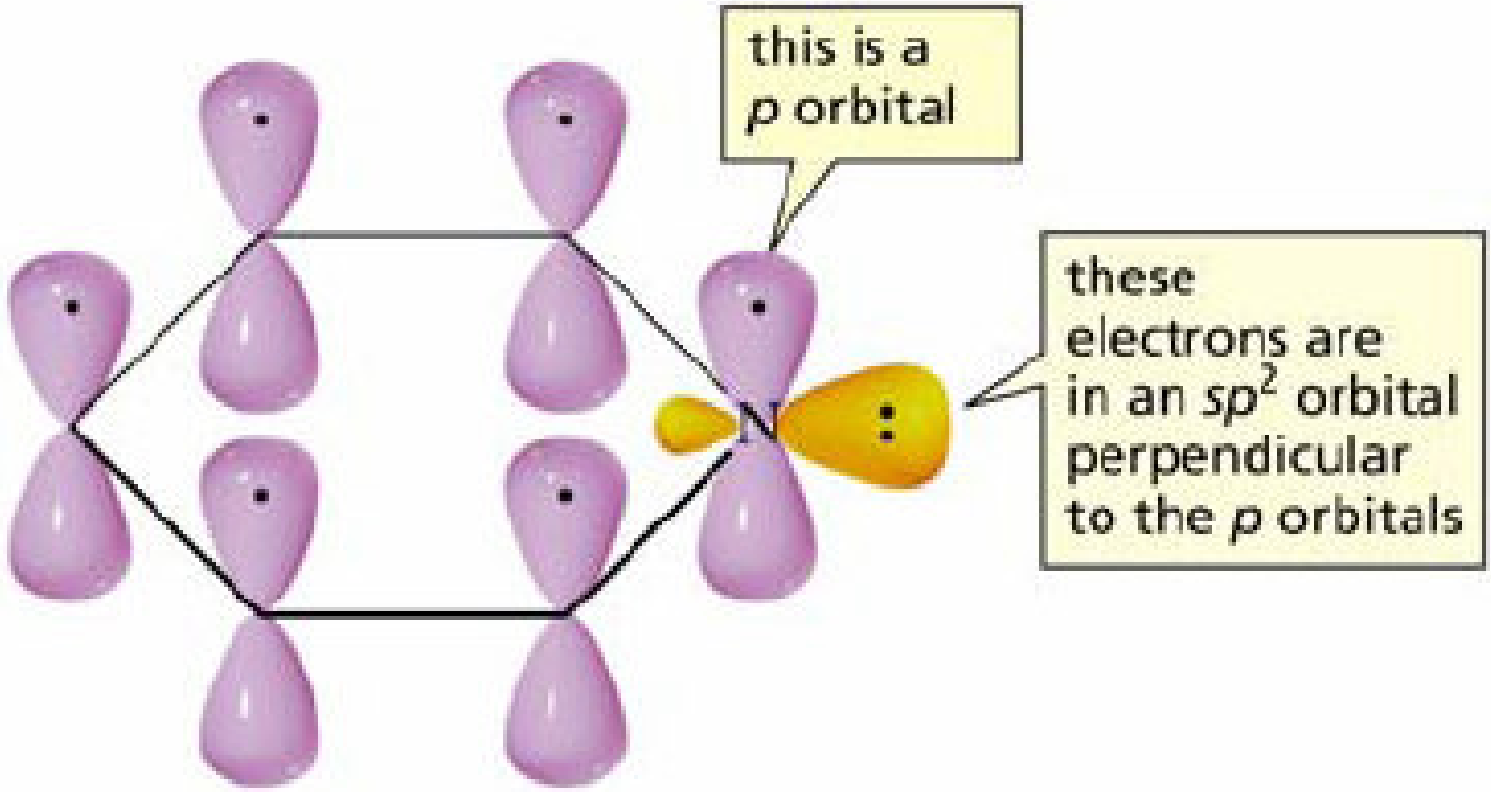
cyclopentadiene

2 pairs of π electrons
not aromatic

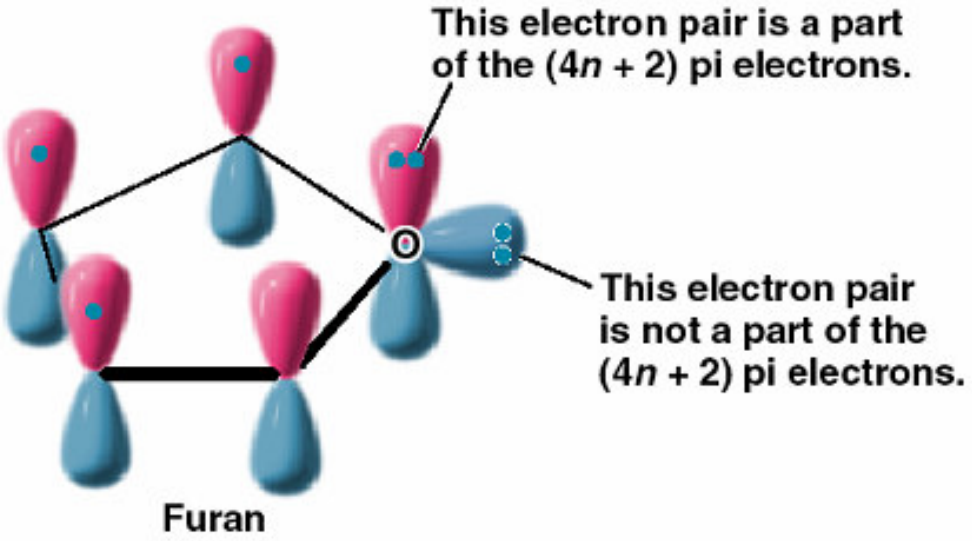
10- Aromaticidade em compostos heterociclicos



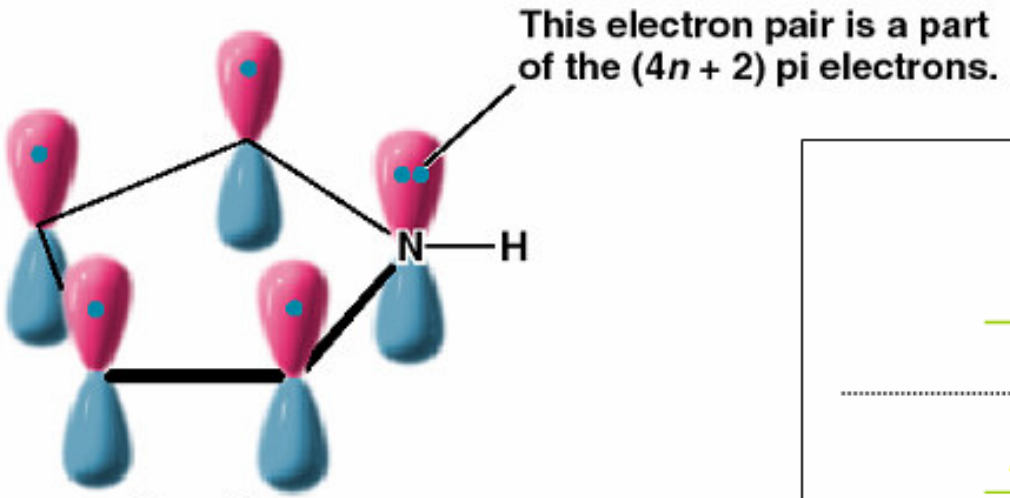
Pyridine Is Aromatic



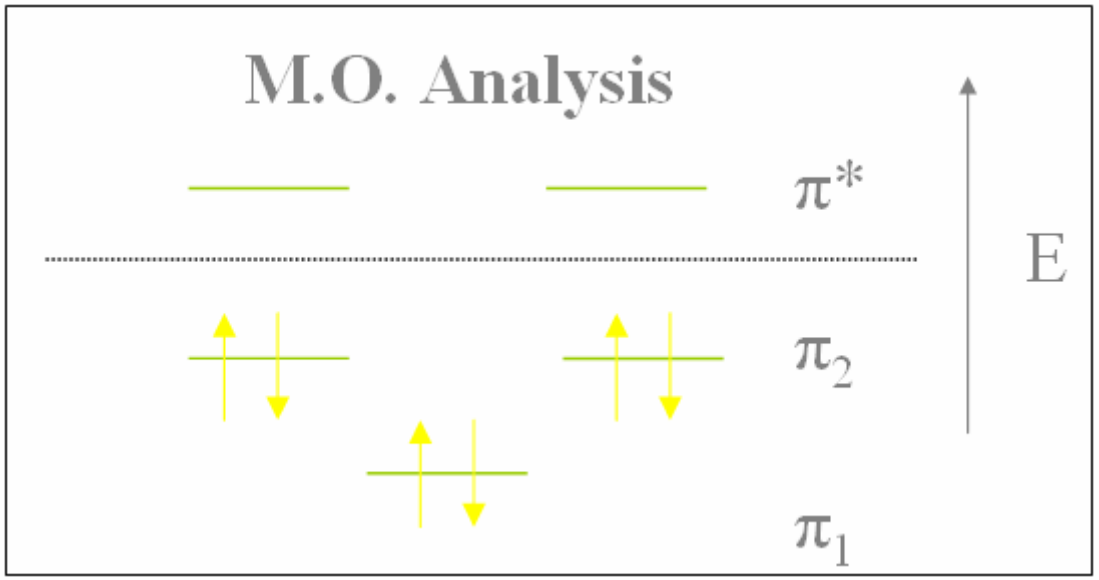
orbital structure of pyridine



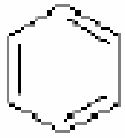
Furan

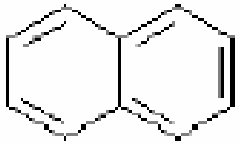


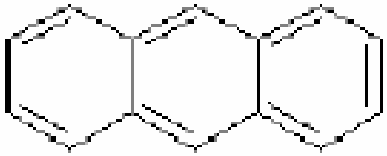
Pyrrole

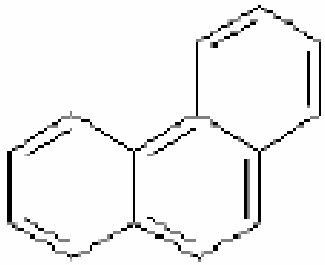


11- Hidrocarbonetos poliaromaticos – HPA's







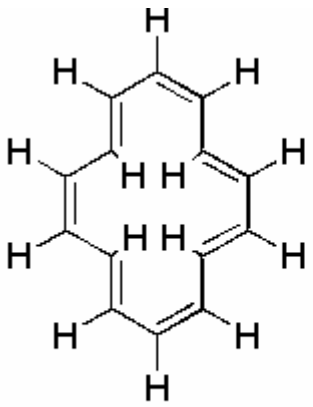


Benzene	Naphthalene	Anthracene	Phenanthrene
152 kJ/mol	255 kJ/mol	347 kJ/mol	381 kJ/mol

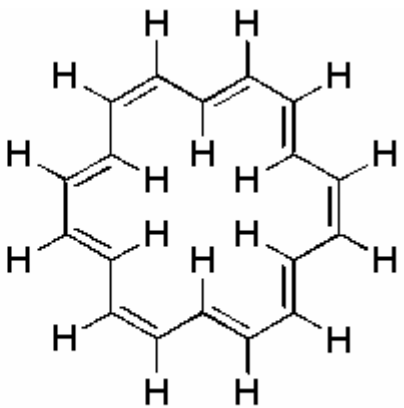
- Energia de ressonancia menor do que o mesmo numero de aneis benzenicos isolados;
- Mais reativos do que o benzeno.

12- Anulenos

- O ciclobutadieno, benzeno, ciclooctatetraeno são os primeiros membros de um grupo denominado de anuleno.
- Uma serie destes compostos já foi sintetizada.

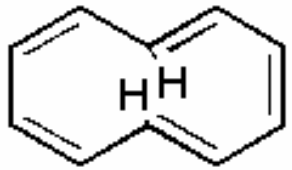


[14]Annulene



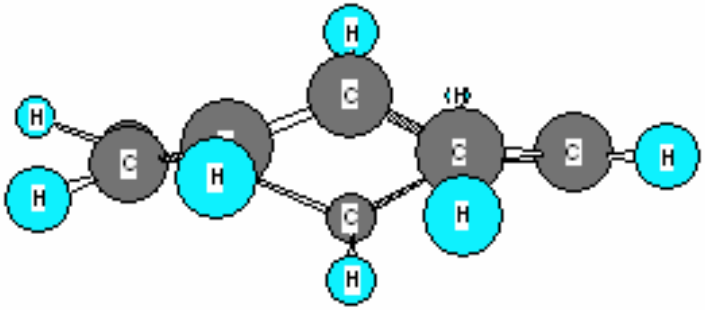
[18]Annulene

Aromaticidade em anulenos - alguns

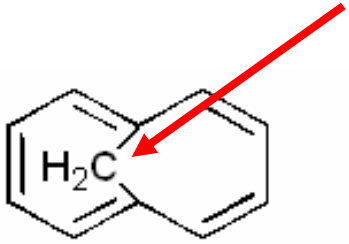


[10]annulene
non-planar

non aromatic

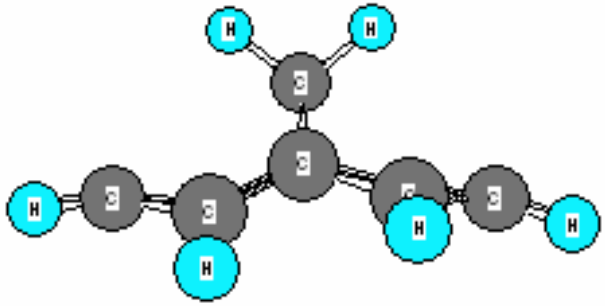


[10]annulene
side view

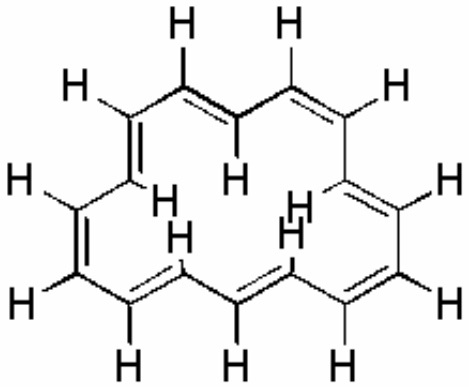


Bridged [10]annulene
planar

aromatic

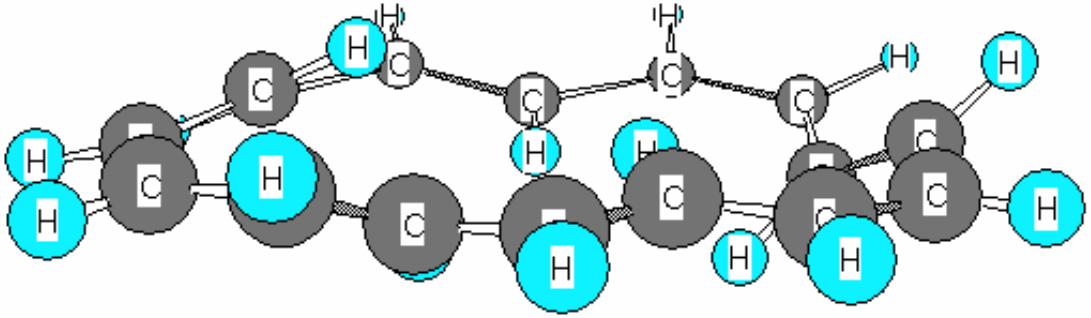


Bridged [10]annulene
side view



[16]annulene
non-planar

non aromatic



[16]annulene
side view