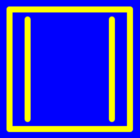
11.18

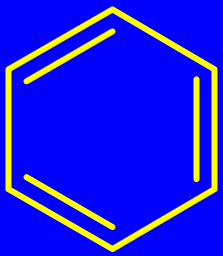
Cyclobutadiene and Cyclooctatetraene

Requirements for Aromaticity

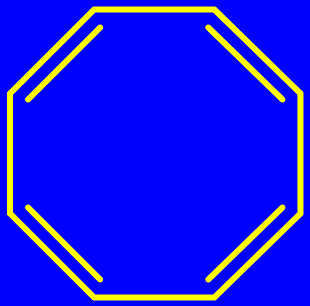
cyclic conjugation is necessary, *but not sufficient*



not
aromatic



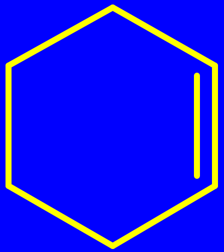
aromatic



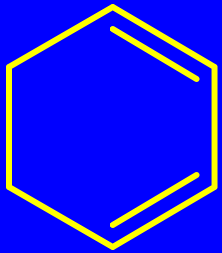
not
aromatic

Heats of Hydrogenation

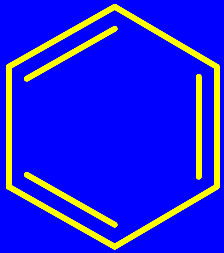
to give cyclohexane (kJ/mol)



120



231

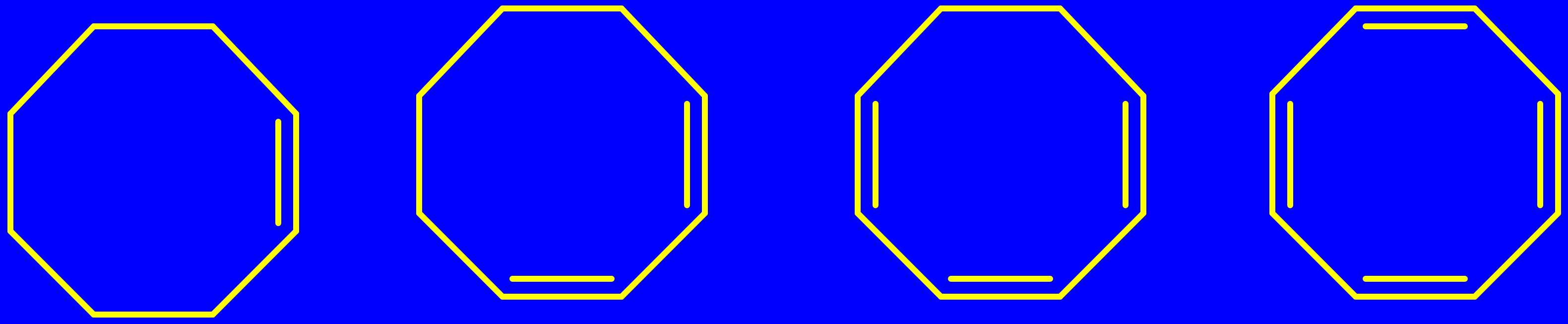


208

heat of hydrogenation of benzene is 152 kJ/mol less than 3 times heat of hydrogenation of cyclohexene

Heats of Hydrogenation

to give cyclooctane (kJ/mol)

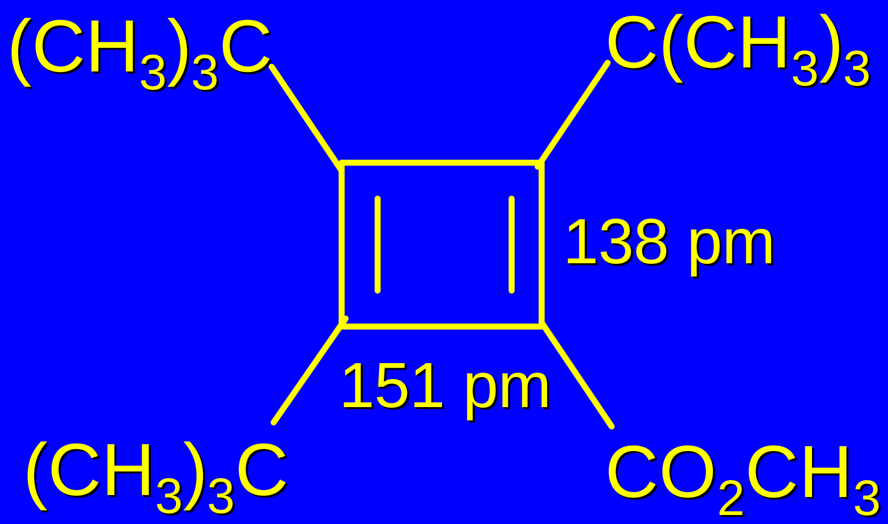


97 205 303 410

heat of hydrogenation of cyclooctatetraene is more than 4 times heat of hydrogenation of cyclooctene

Structure of Cyclobutadiene

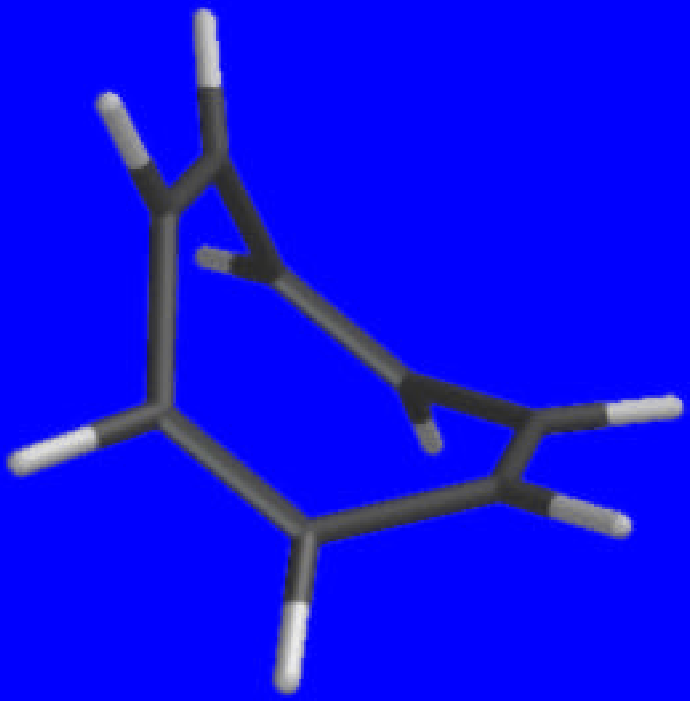
structure of a stabilized derivative is characterized by alternating short bonds and long bonds



Structure of Cyclooctatetraene

cyclooctatetraene is not planar

has alternating long (146 pm)
and short (133 pm) bonds



Conclusion

there must be some factor in addition to cyclic conjugation that determines whether a molecule is aromatic or not

11.19

Hückel's Rule:

Annulenes

the additional factor that influences aromaticity is the number of *p* electrons

Hückel's Rule

among planar, monocyclic, completely conjugated polyenes, only those with 4*n* + 2 π electrons possess special stability (are aromatic)

n	4*n*+2
0	2
1	6
2	10
3	14
4	18

Hückel's Rule

among planar, monocyclic, completely conjugated polyenes, only those with 4*n* + 2 π electrons possess special stability (are aromatic)

n	4*n*+2	
0	2	
1	6	benzene!
2	10	
3	14	
4	18	

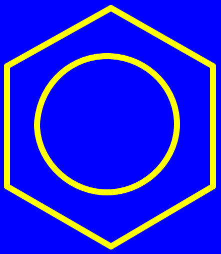
Hückel's Rule

Hückel restricted his analysis to planar, completely conjugated, monocyclic polyenes

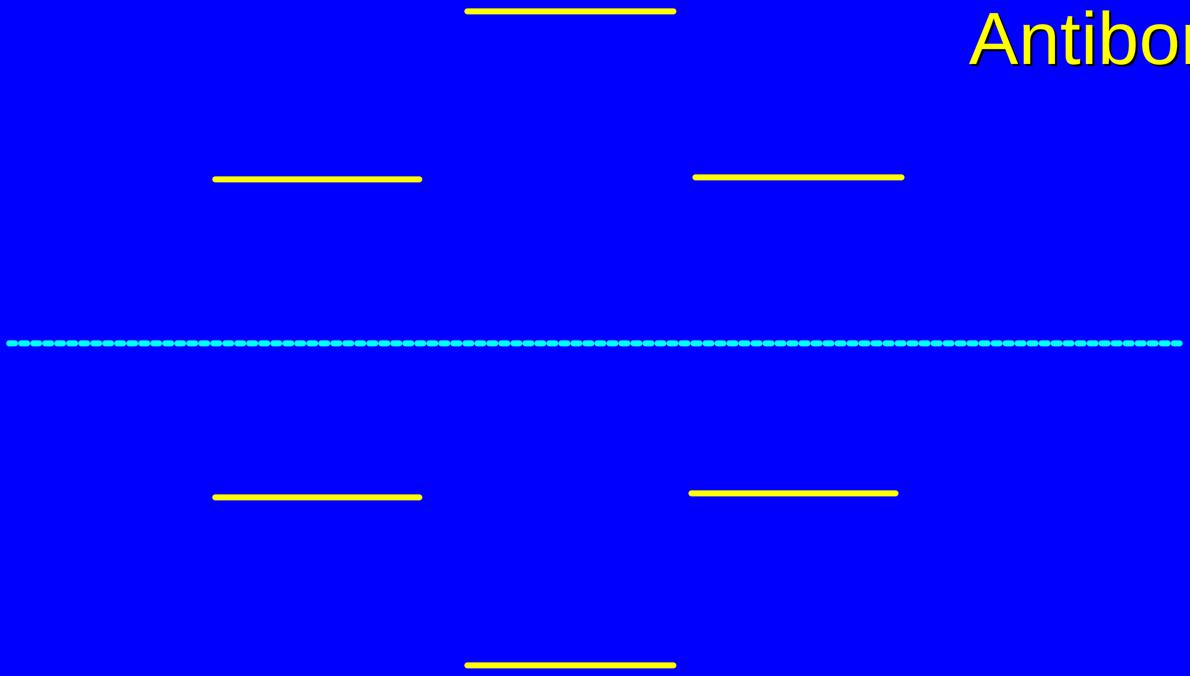
he found that the *p* molecular orbitals of these compounds had a distinctive pattern

one *p* orbital was lowest in energy, another was highest in energy, and the others were arranged in pairs between the highest and the lowest

p-MOs of Benzene



Benzene



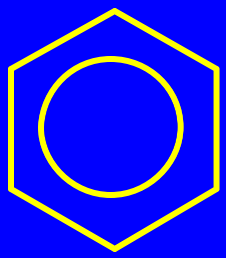
Antibonding

Bonding

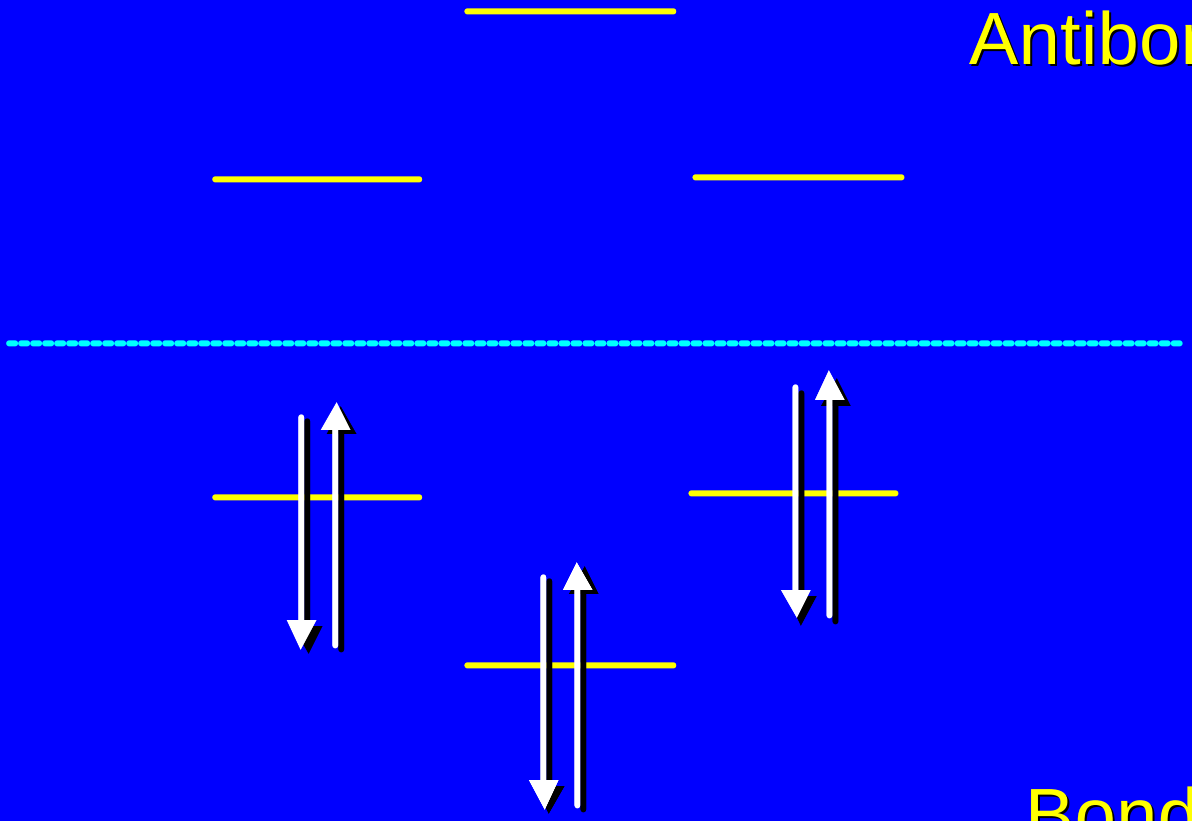
6 *p* orbitals give 6 *p* orbitals

3 orbitals are bonding; 3 are antibonding

p-MOs of Benzene



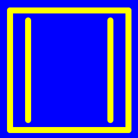
Benzene



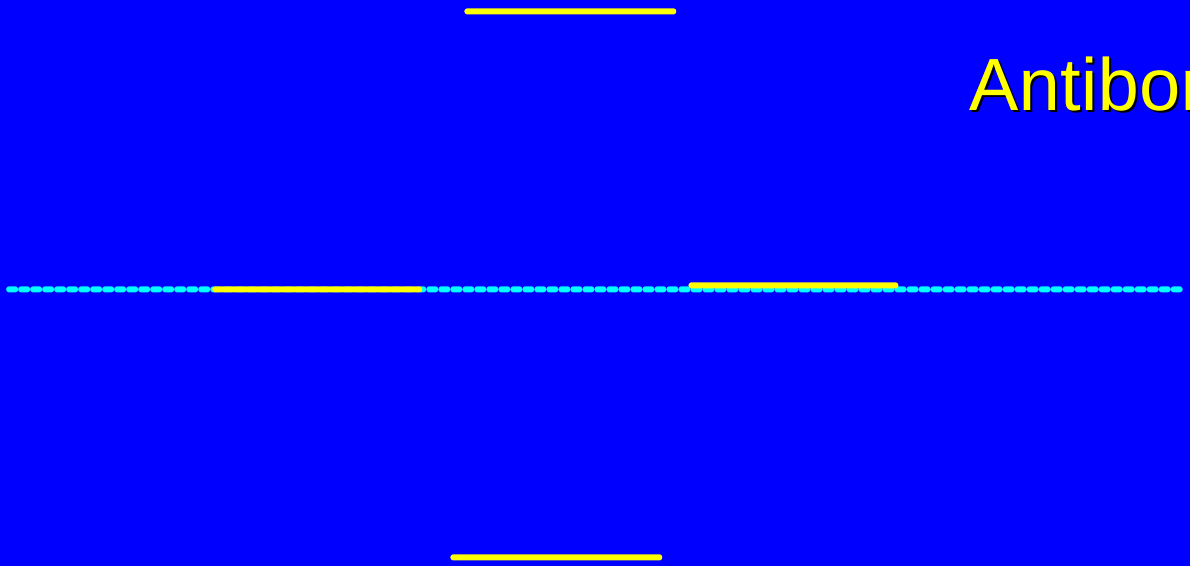
6 *p* electrons fill all of the bonding orbitals

all *p* antibonding orbitals are empty

p-MOs of Cyclobutadiene (square planar)



Cyclobutadiene



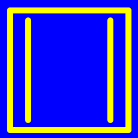
Antibonding

Bonding

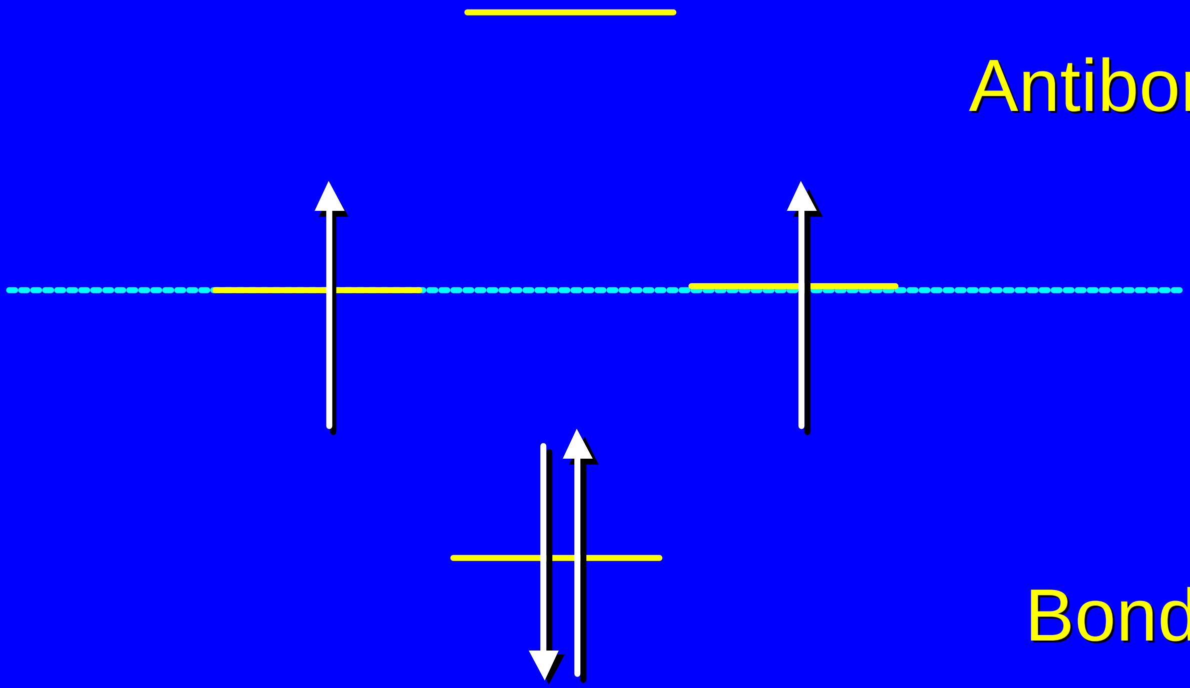
4 *p* orbitals give 4*p* orbitals

1 orbital is bonding, one is antibonding, and 2 are nonbonding

p-MOs of Cyclobutadiene
(square planar)



Cyclo-
butadiene

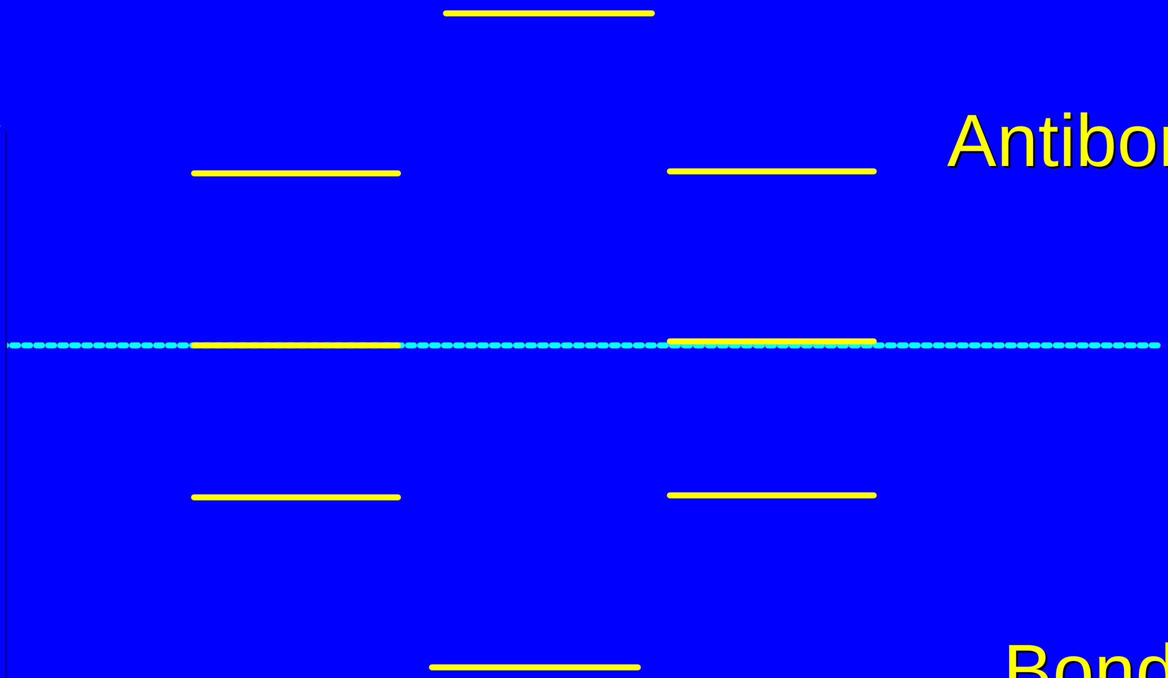


Antibonding

Bonding

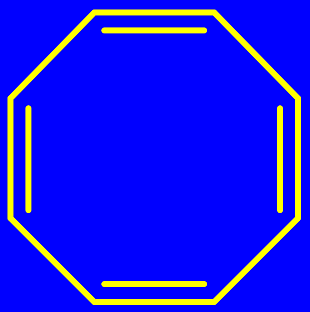
4 *p* electrons; bonding orbital is filled; other 2 *p* electrons singly occupy two nonbonding orbitals

p-MOs of Cyclooctatetraene (square planar)



Antibonding

Bonding

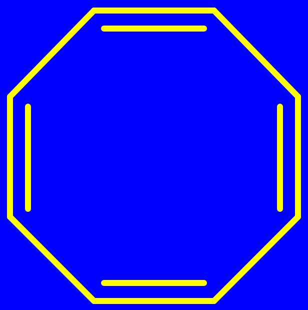


Cyclo-
octatetraene

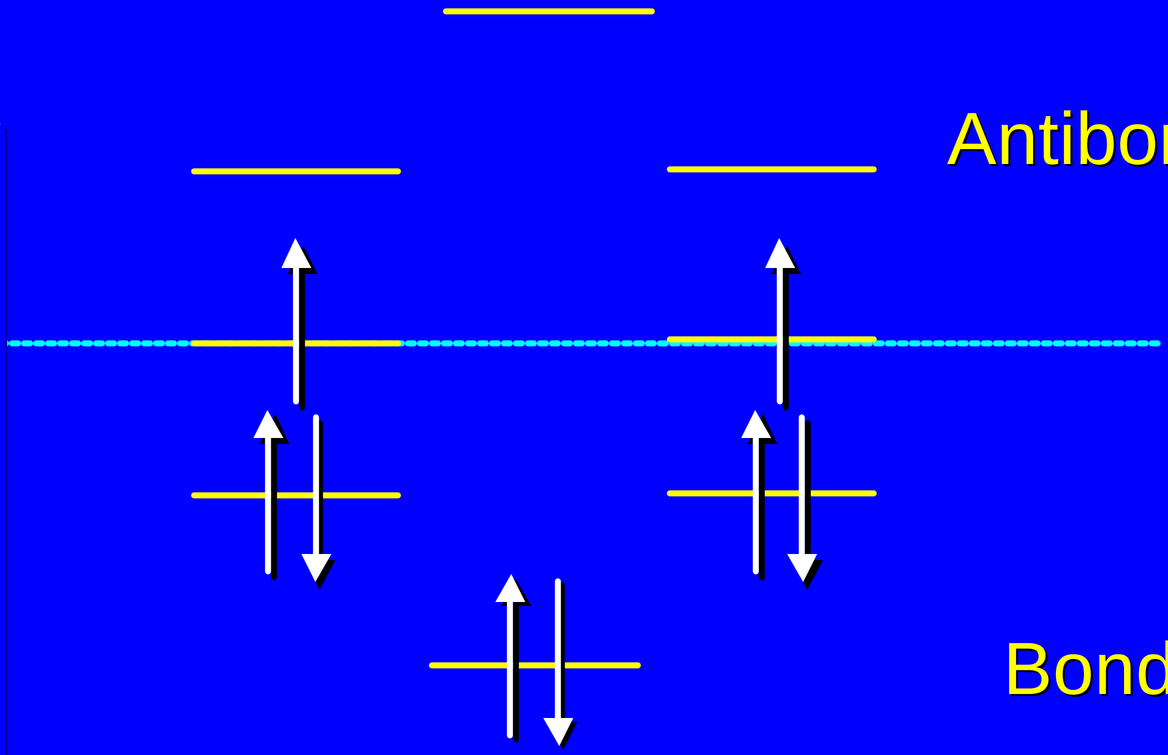
8 *p* orbitals give 8 *p* orbitals

3 orbitals are bonding, 3 are antibonding, and 2 are nonbonding

p-MOs of Cyclooctatetraene (square planar)



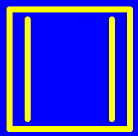
Cyclo-octatetraene



8 *p* electrons; 3 bonding orbitals are filled; 2 nonbonding orbitals are each half-filled

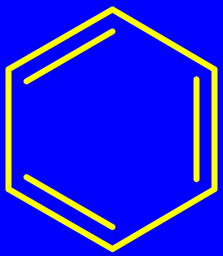
p-Electron Requirement for Aromaticity

4 *p* electrons



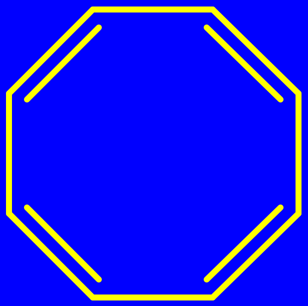
not
aromatic

6 *p* electrons



aromatic

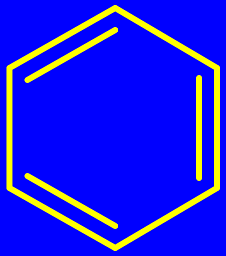
8 *p* electrons



not
aromatic

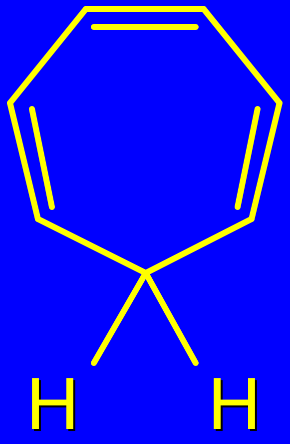
Completely Conjugated Polyenes

6 *p* electrons;
completely conjugated



aromatic

6 *p* electrons;
not completely
conjugated

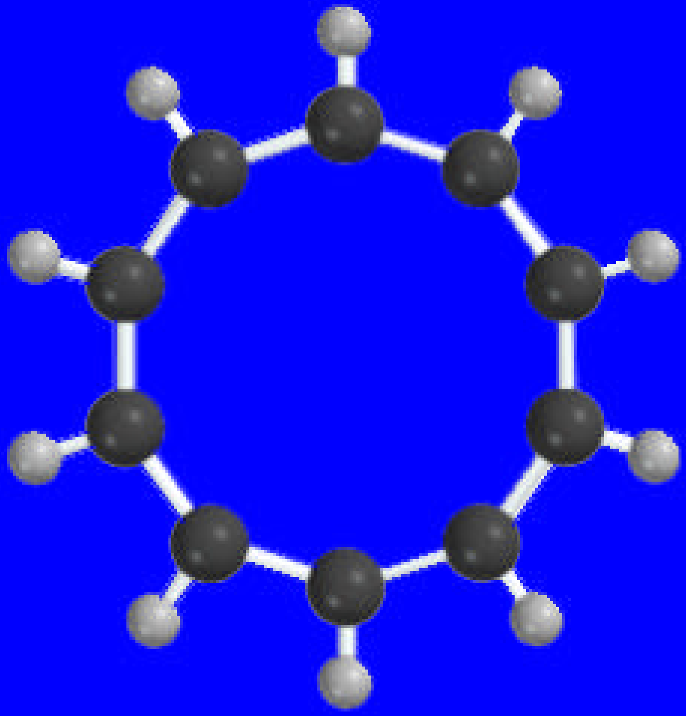


not
aromatic

Annulenes

Annulenes are planar, monocyclic, completely conjugated polyenes. That is, they are the kind of hydrocarbons treated by Hückel's rule.

[10]Annulene



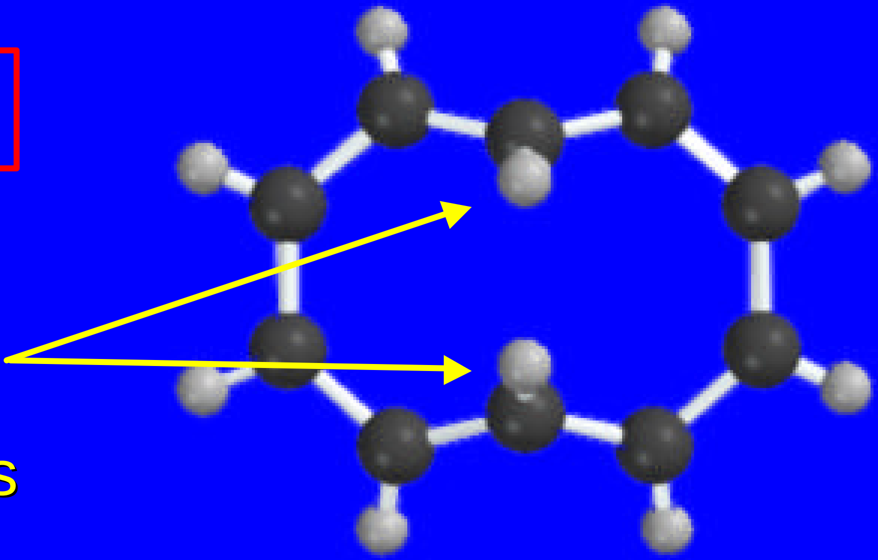
predicted to be aromatic by Hückel's rule, but too much angle strain when planar and all double bonds are cis

10-sided regular polygon has angles of 144°

[10]Annulene

incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity

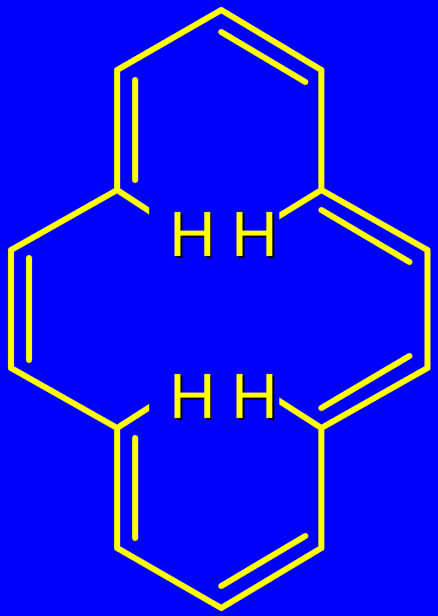
[10]Annulene



van der Waals
strain between
these two hydrogens

incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity

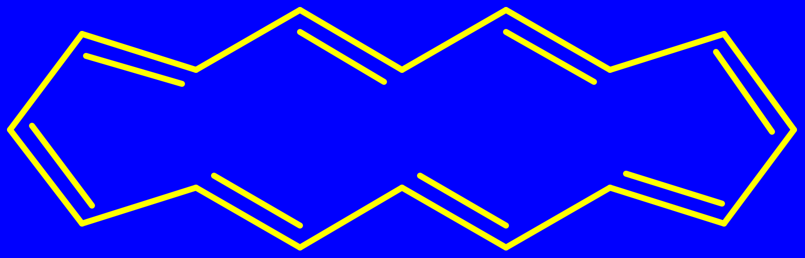
[14]Annulene



14 *p* electrons satisfies Hückel's rule

van der Waals strain between hydrogens inside the ring

[16]Annulene

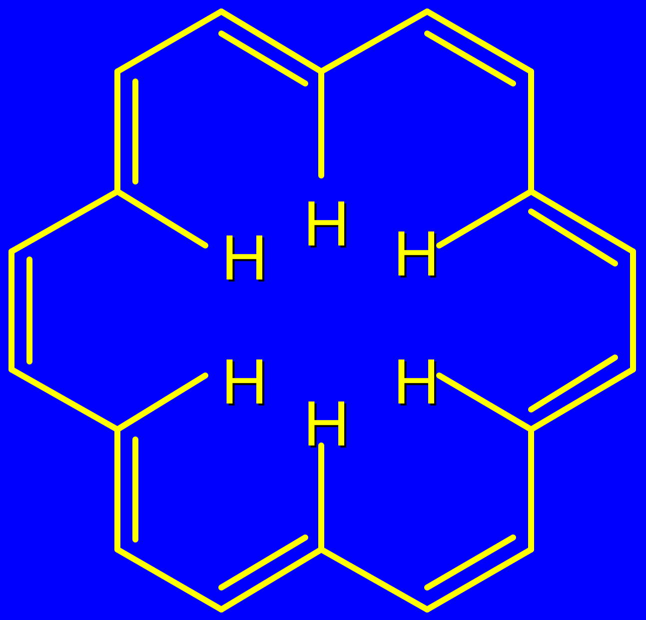


16 *p* electrons does not satisfy Hückel's rule

alternating short (134 pm) and long (146 pm) bonds

not aromatic

[18]Annulene



18 *p* electrons satisfies Hückel's rule

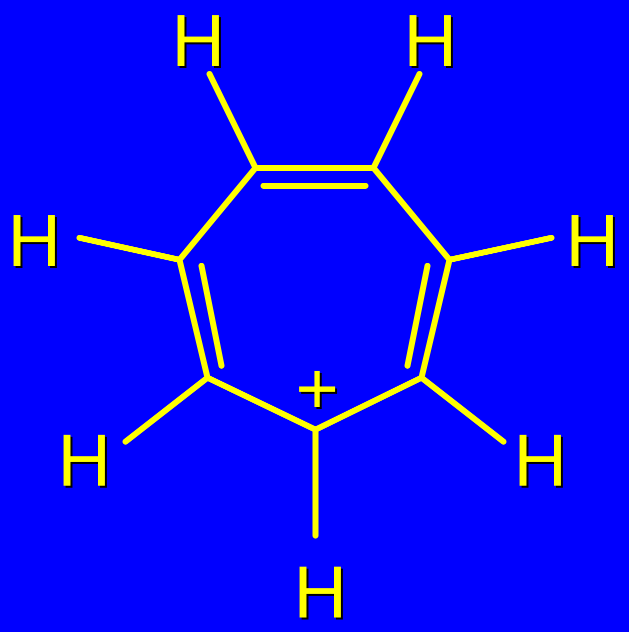
resonance energy = 418 kJ/mol

bond distances range between 137-143 pm

11.20

Aromatic Ions

Cycloheptatrienyl Cation



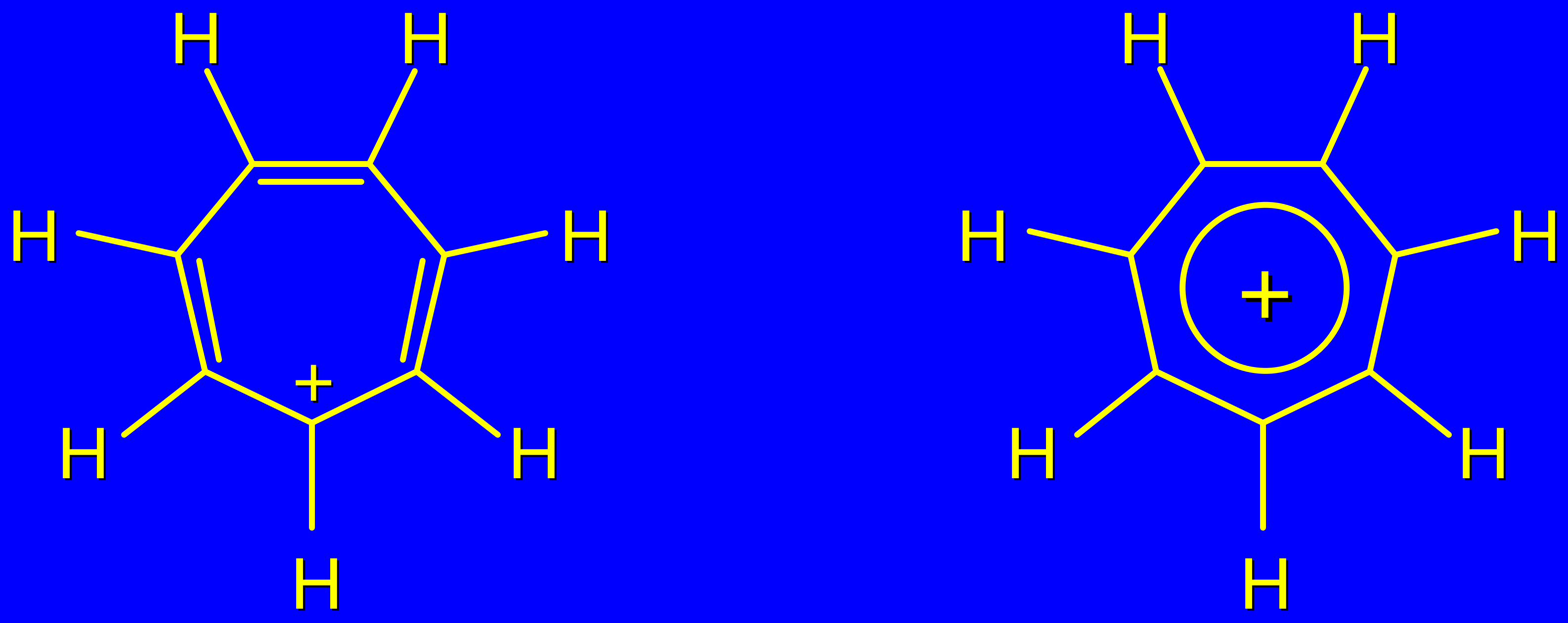
6 *p* electrons delocalized
over 7 carbons

positive charge dispersed
over 7 carbons

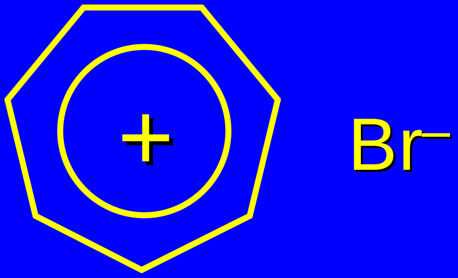
very stable carbocation

also called tropylium cation

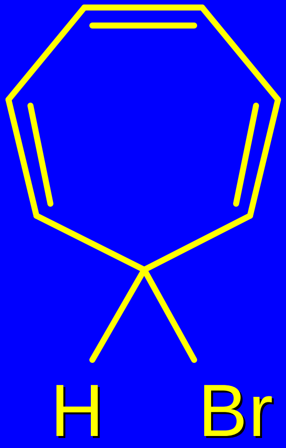
Cycloheptatrienyl Cation



Cycloheptatrienyl Cation



Ionic

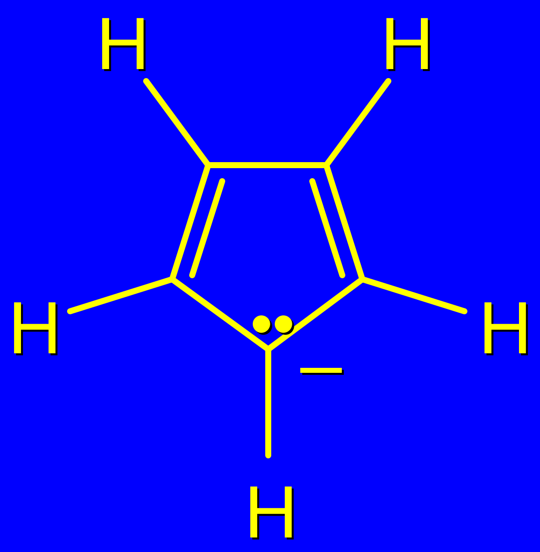


Covalent

Tropylium cation is so stable that tropylium bromide is ionic rather than covalent.

mp 203 °C; soluble in water; insoluble in diethyl ether

Cyclopentadienide Anion

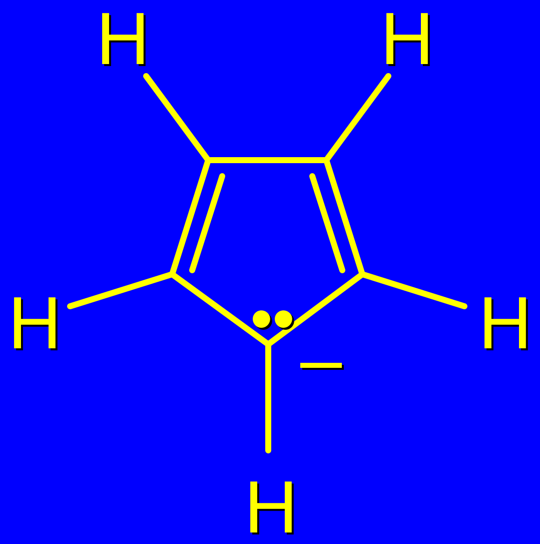


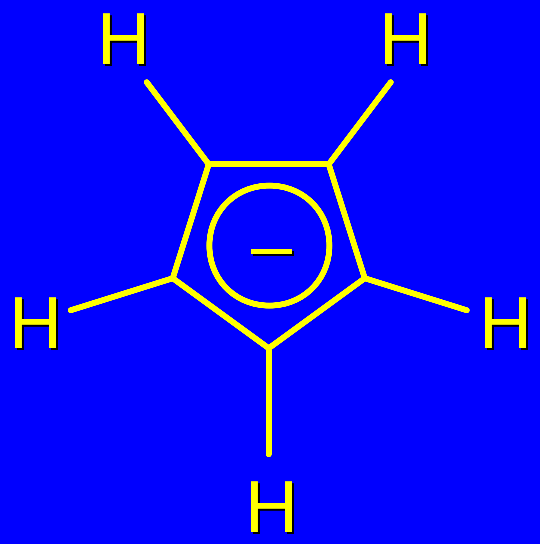
6 *p* electrons delocalized
over 5 carbons

negative charge dispersed
over 5 carbons

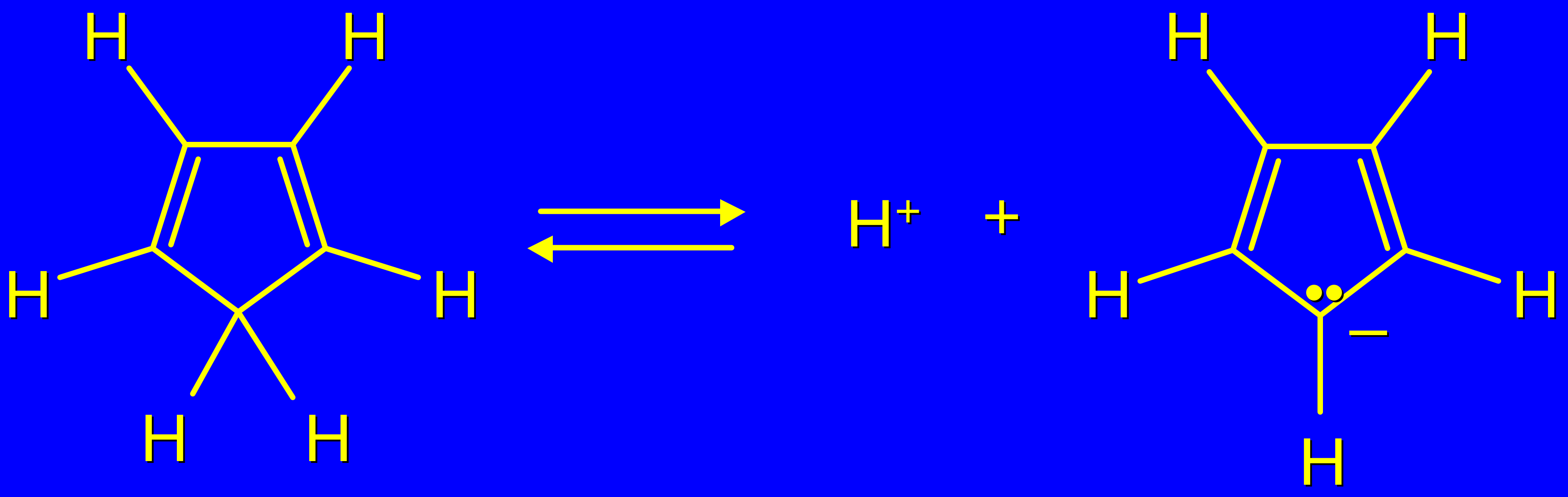
stabilized anion

Cyclopentadienide Anion





Acidity of Cyclopentadiene



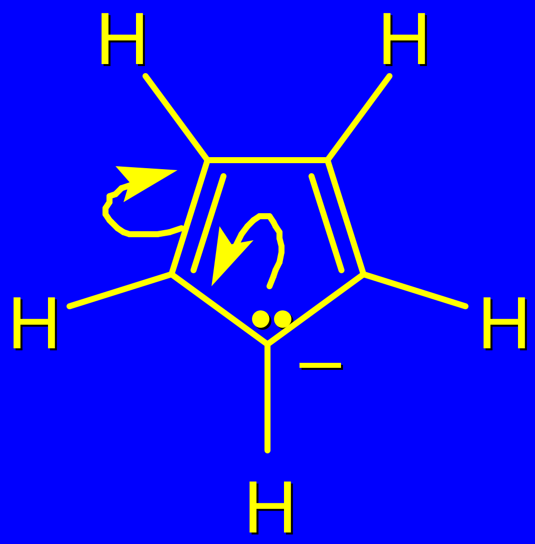
$\mathrm{p}K_a = 16$

$K_a = 10^{-16}$

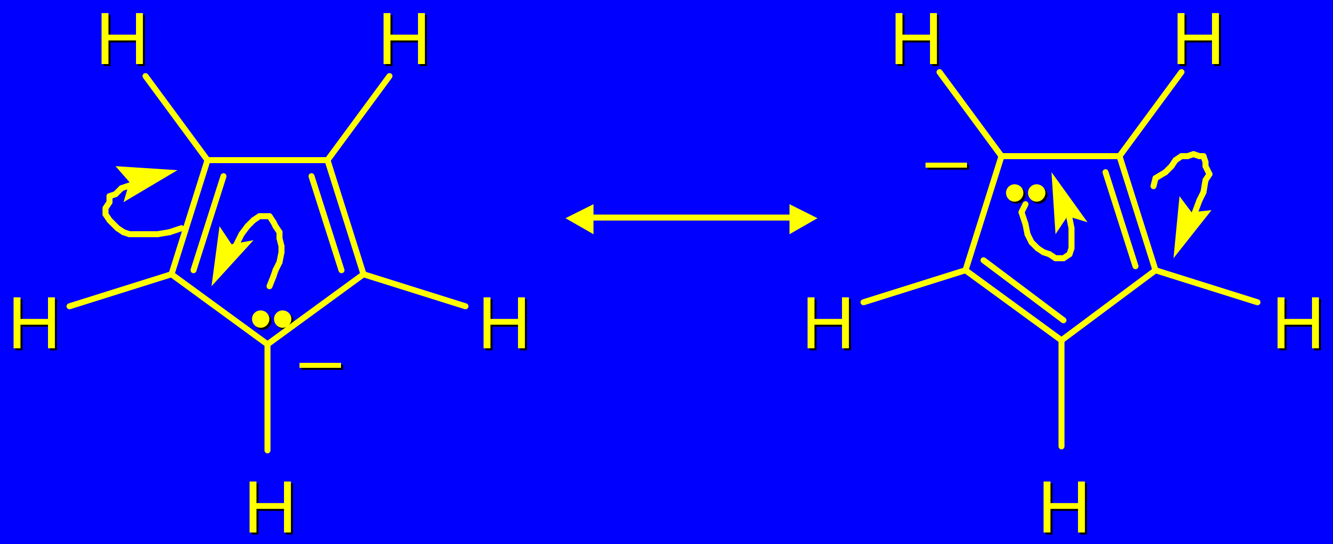
Cyclopentadiene is unusually acidic for a hydrocarbon.

Increased acidity is due to stability of cyclopentadienide anion.

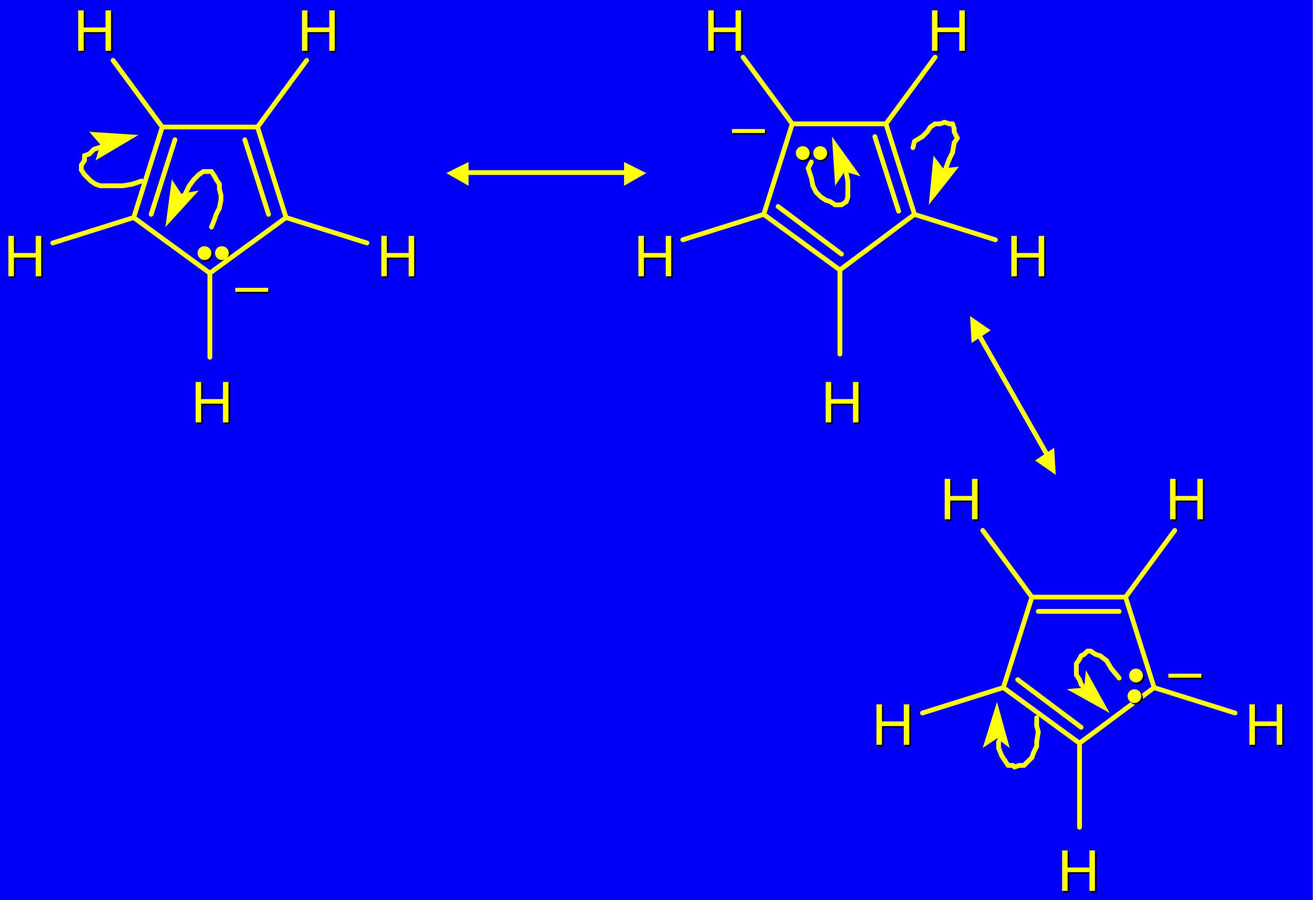
Electron Delocalization in Cyclopentadienide Anion



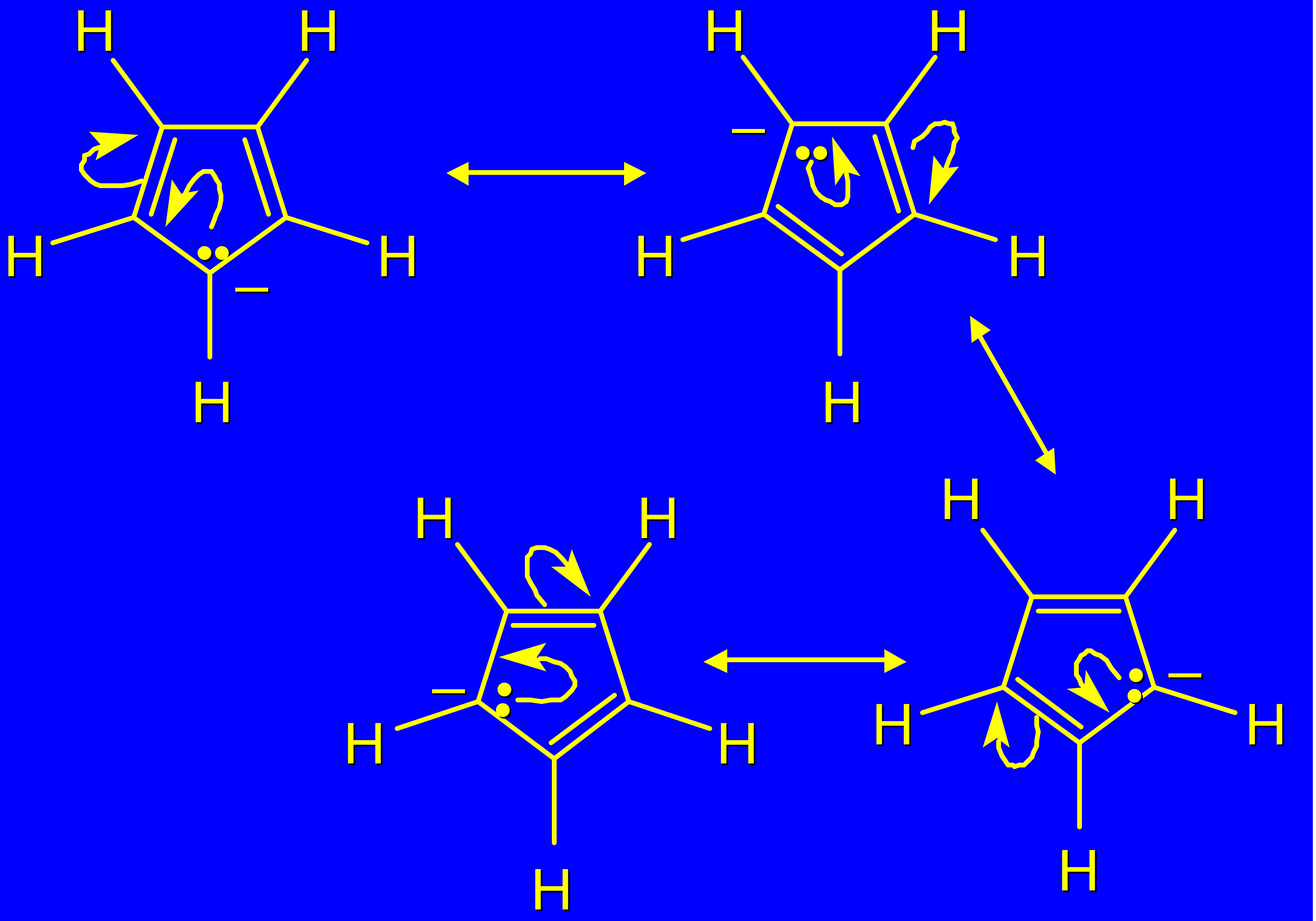
Electron Delocalization in Cyclopentadienide Anion



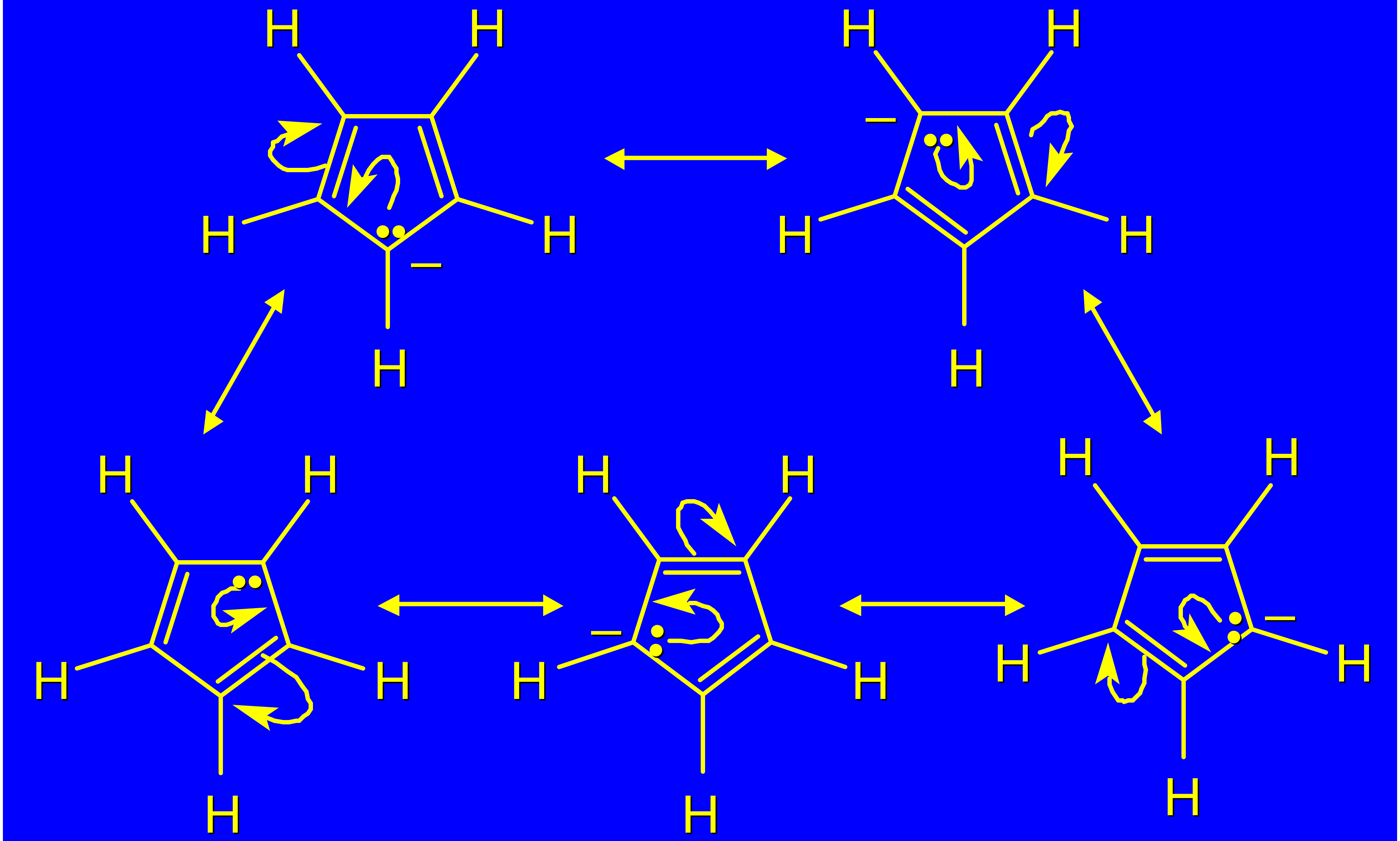
Electron Delocalization in Cyclopentadienide Anion



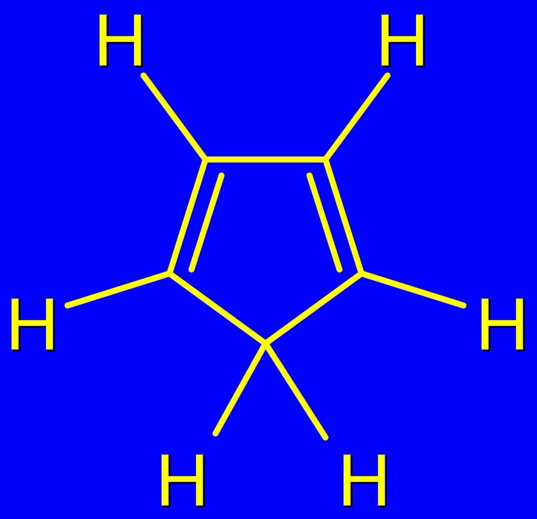
Electron Delocalization in Cyclopentadienide Anion



Electron Delocalization in Cyclopentadienide Anion

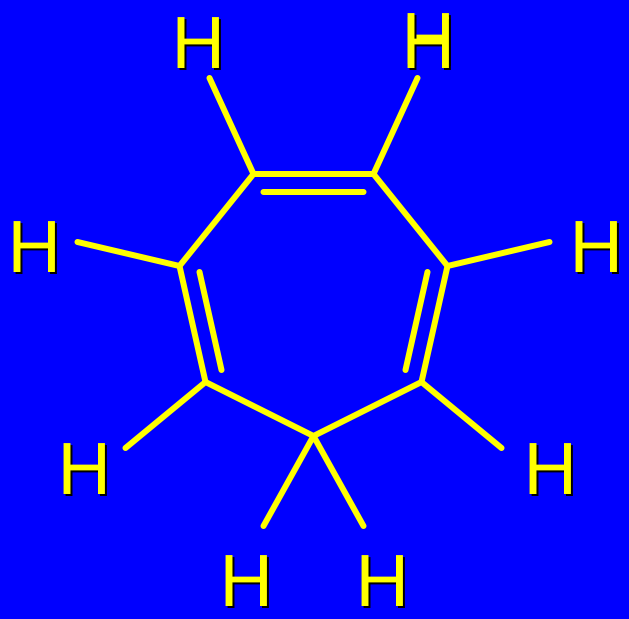


Compare Acidities of Cyclopentadiene and Cycloheptatriene



pK_a = 16

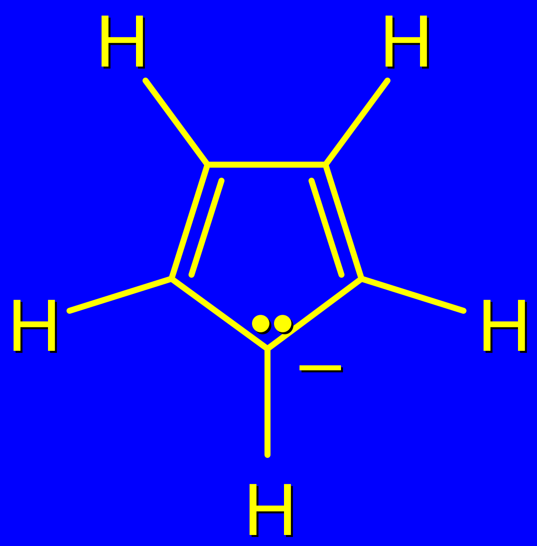
K_a = 10^{-16}



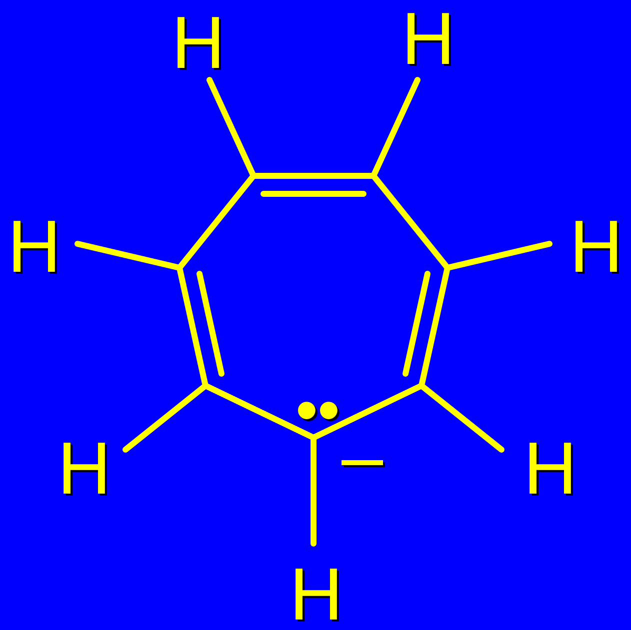
pK_a = 36

K_a = 10^{-36}

Compare Acidities of Cyclopentadiene and Cycloheptatriene

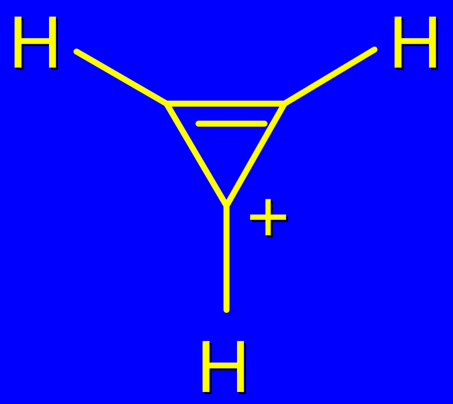


Aromatic anion
6 *p* electrons

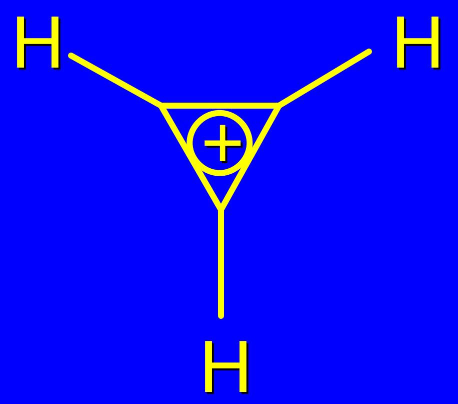


Anion not aromatic
8 *p* electrons

Cyclopropenyl Cation



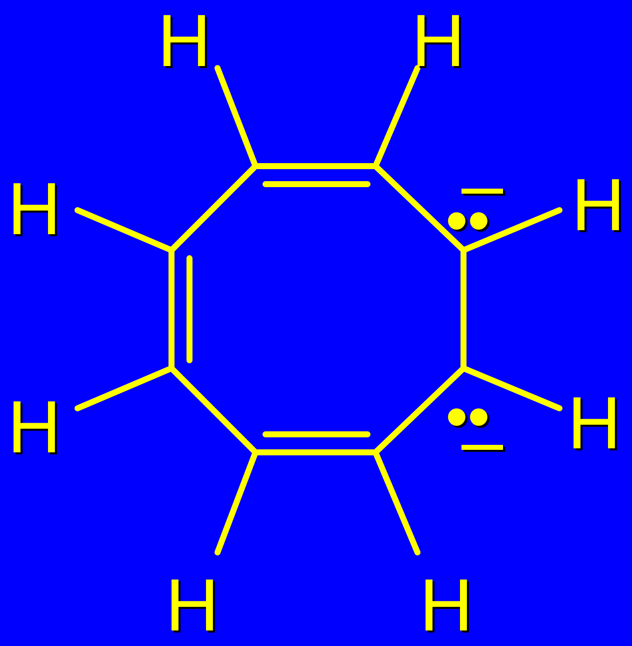
also written as



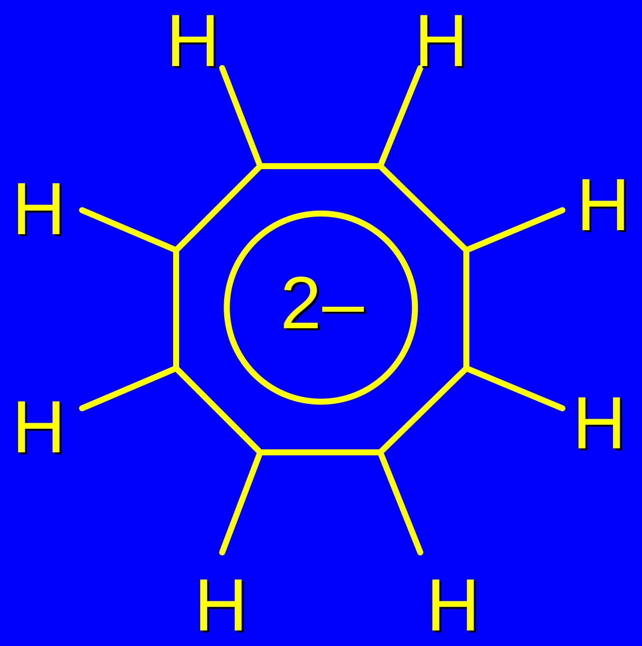
$n = 0$

$4n + 2 = 2$ *p* electrons

Cyclooctatetraene Dianion



also
written as



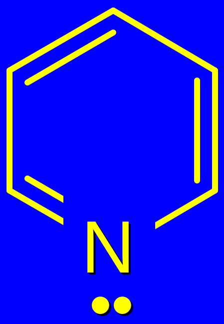
$n = 2$

$4n + 2 = 10$ *p* electrons

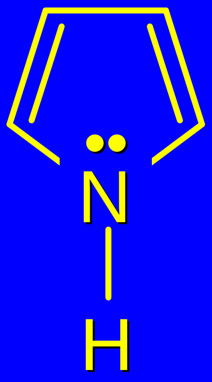
11.21

Heterocyclic Aromatic Compounds

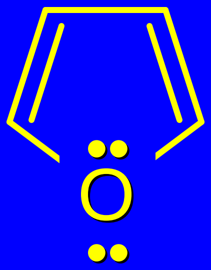
Examples



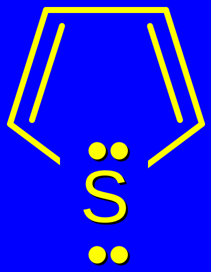
Pyridine



Pyrrole

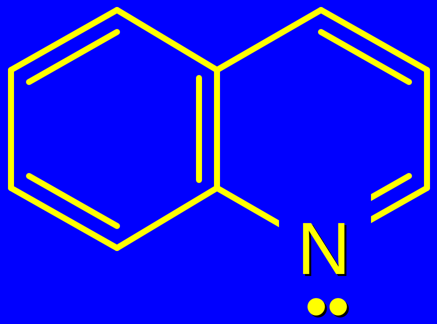


Furan

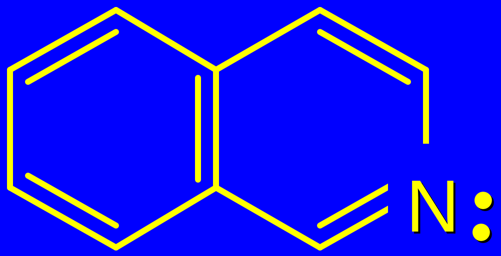


Thiophene

Examples



Quinoline



Isoquinoline

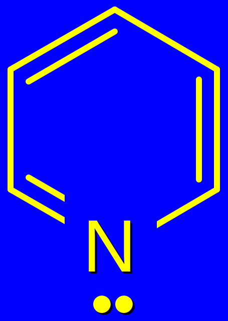
11.22

Heterocyclic Aromatic Compounds

and

Hückel's Rule

Pyridine



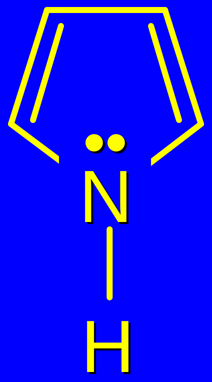
6 *p* electrons in ring

lone pair on nitrogen is in an

sp^2 hybridized orbital;

not part of *p* system of ring

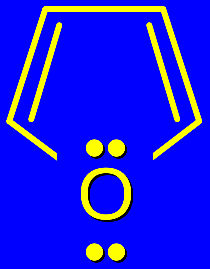
Pyrrole



lone pair on nitrogen must be part of ring *p* system if ring is to have 6 *p* electrons

lone pair must be in a *p* orbital in order to overlap with ring *p* system

Furan



two lone pairs on oxygen

one pair is in a *p* orbital and is part of ring *p* system; other is in an *sp^2* hybridized orbital and is not part of ring *p* system