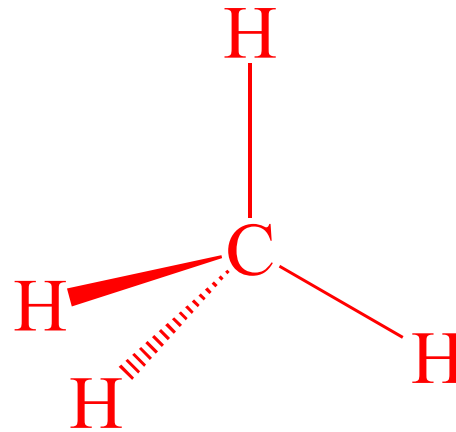
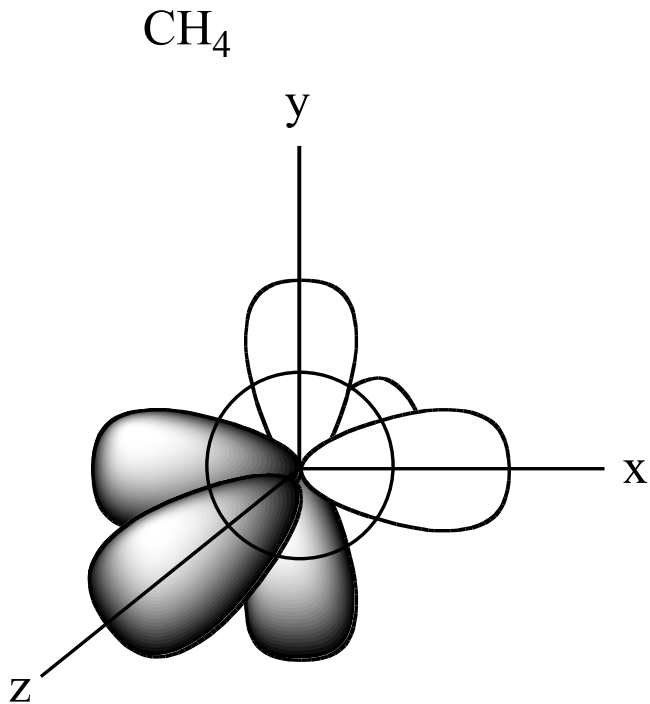
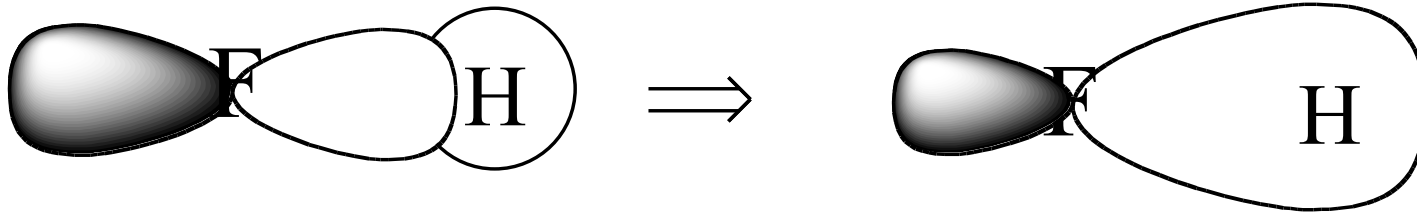


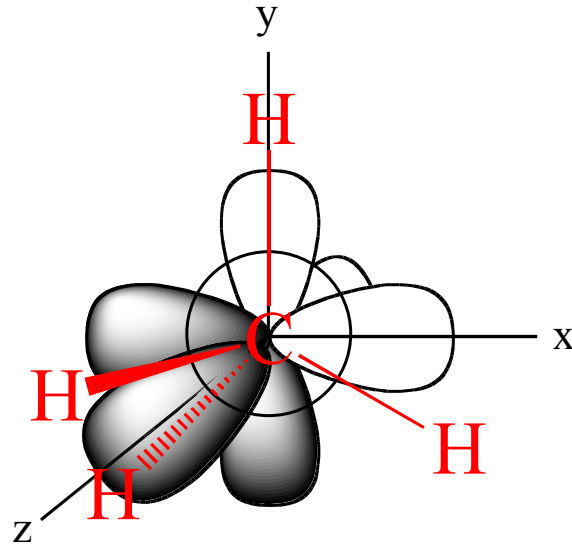
Bonding

We can imagine the HF molecule arising from the following orbital overlap...

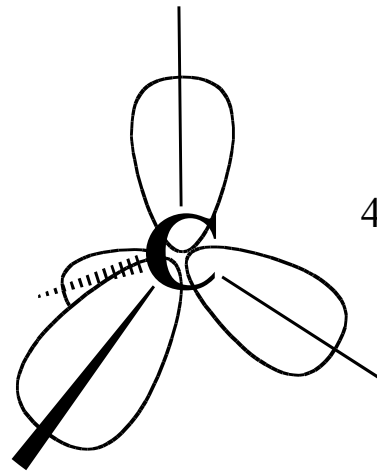
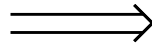
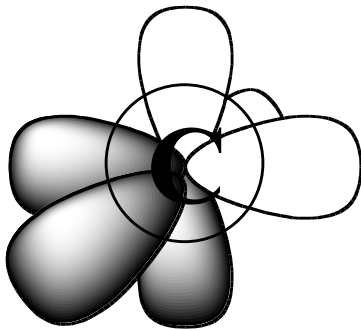


Bonding

Orbital hybridization:



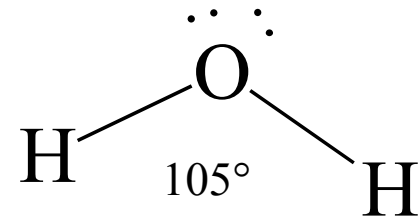
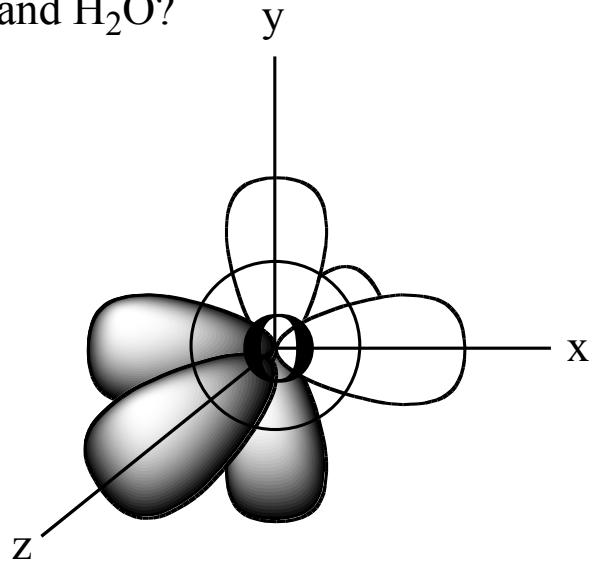
CH₄ - tetrahedral



4 sp³ hybrid orbitals.

Bonding

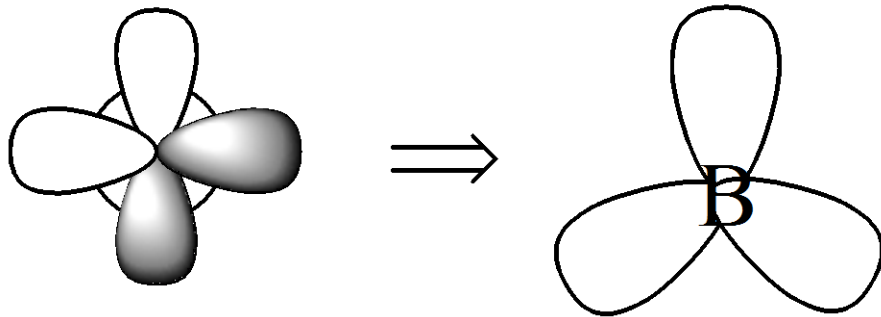
and H₂O?



Bonding

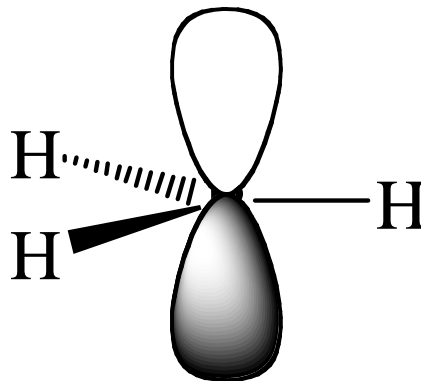
BH_3 - trigonal planar

We need three hybrid orbitals to form the B—H bonds.



Three sp^2 hybrid orbitals can be formed. They have spatial components in one plane - that of the atomic p orbitals from which they are hybridized.

Where is the unhybridized orbital?

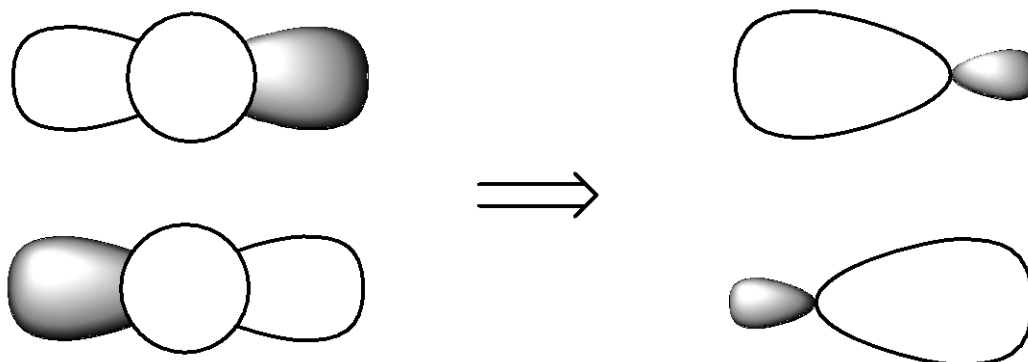


Bonding

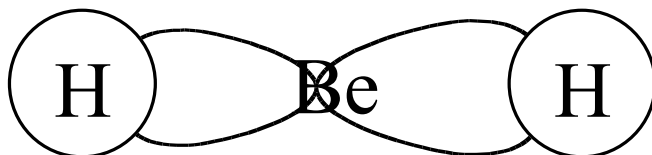
BeH₂

This is a linear molecule. Be has a 2s and three 2p orbitals. It needs to use two of these orbitals to form two bonds to the H atoms. Consider the superimposition of the 2s and 2p_x orbitals on the Be atom...

Two possible combinations...



Note that the two hybrid orbitals share the spatial (along the x axis) and nodal properties of the atomic orbitals from which they are hybridized.



The remaining atomic 2p orbitals are still there but vacant.

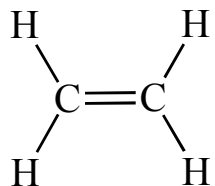
Bonding

The hybridization of any atom can be determined from its geometry:

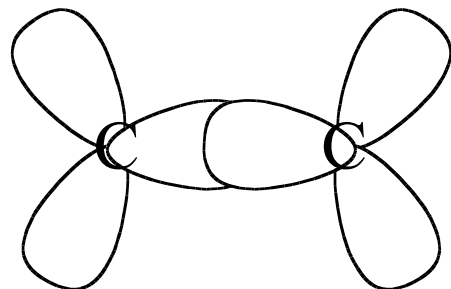
Steric No.	Geometry	Hybridization	Unhybridized
2			
3			
4			

Bonding

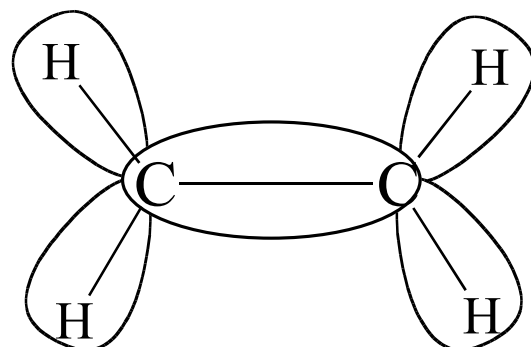
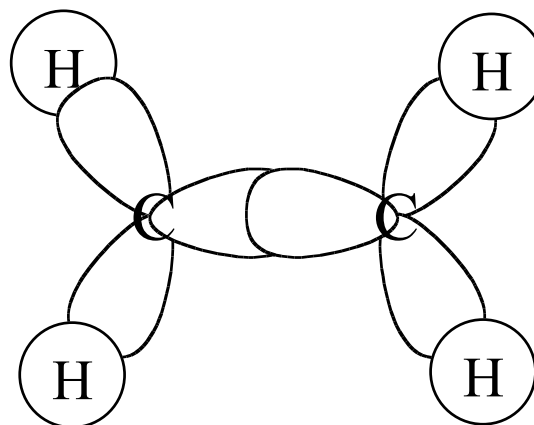
Bonding in Ethylene



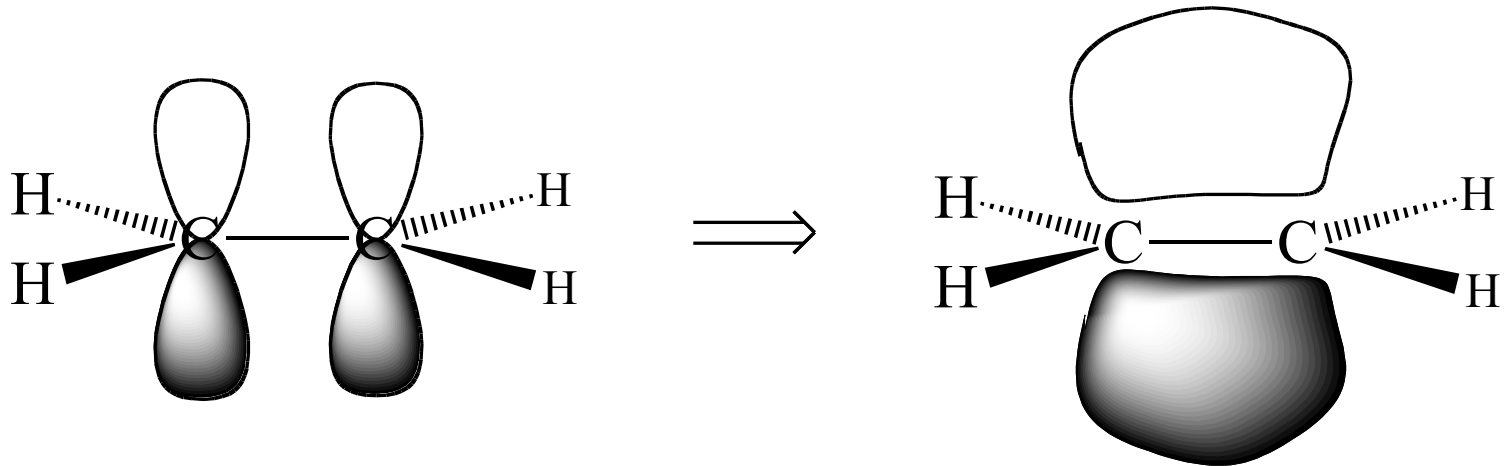
12 valence electrons



C—C σ bond.

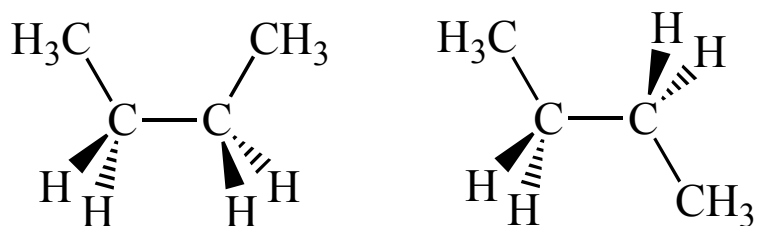


The σ bond framework of ethylene.

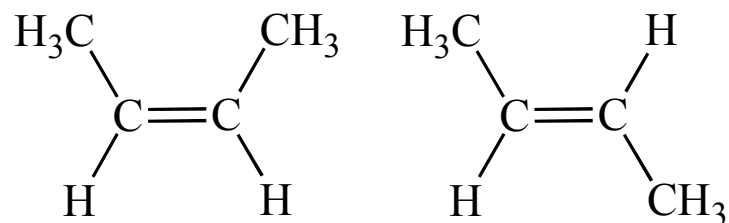


This type of bond which results from the parallel overlap of atomic p orbitals has different symmetry than the σ bond. We call it a π bond.

For a π bond to exist, the atomic p orbitals must be parallel. One critically important result of this is that, unlike σ bonds, free rotation about the bond is no longer possible without breaking the π bond. This takes substantial energy.



Different conformations
of the molecule butane.

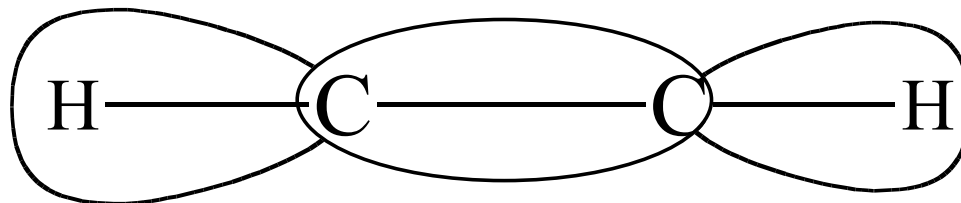
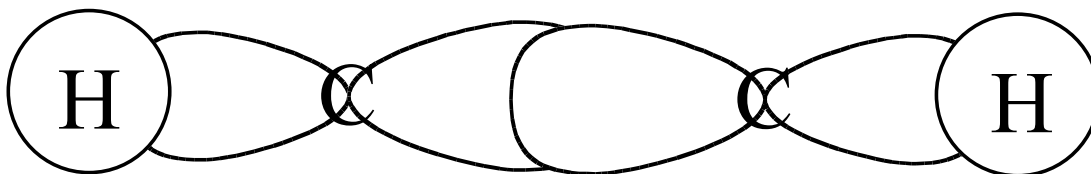


Different molecules: cis-2-
butene and trans-2-butene.

Bonding in Acetylene

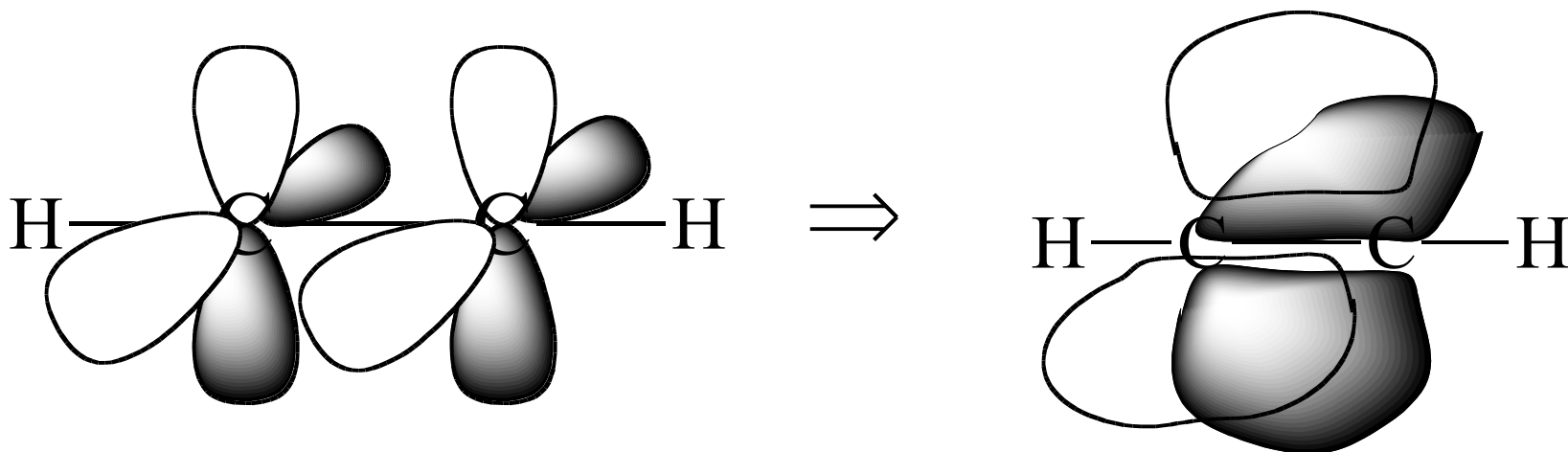


Each C atom is sp hybridized...



The σ bond framework.

Each C atom has TWO unhybridized atomic p orbitals...



Resulting in two π bonds, mutually perpendicular.

Bonding

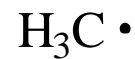
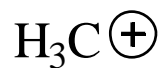
Bond Properties

Bond Length and Bond Strength

Bond	Length (nm)	Strength (kJ/mol)	Bond	Length (nm)	Strength (kJ/mol)
C—C	0.153	347 (83)	C—N	0.147	305 (73)
C=C	0.131	611 (146)	C=N	0.128	615(147)
C≡C	0.118	837 (200)	C≡N	0.114	891(213)
C—H	0.109	414 (99)	C—F	0.140	485(116)
C—O	0.143	360 (86)	C—Cl	0.179	339 (81)
C=O	0.121	740(177)	C—Br	0.197	285 (68)
C—S	0.182	255 (61)	C—I	0.216	218 (52)

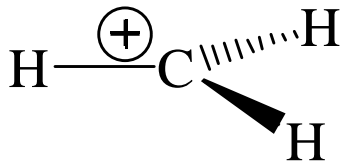
Bonding

Reactive Carbon-centered Intermediates

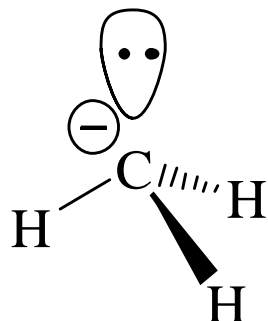


Steric
Number

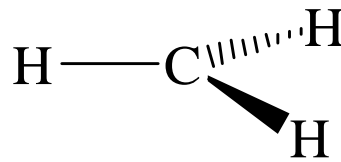
Hybridization



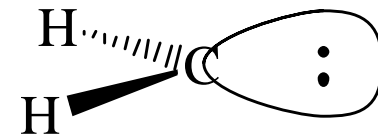
Carbocation



Carbanion



Radical

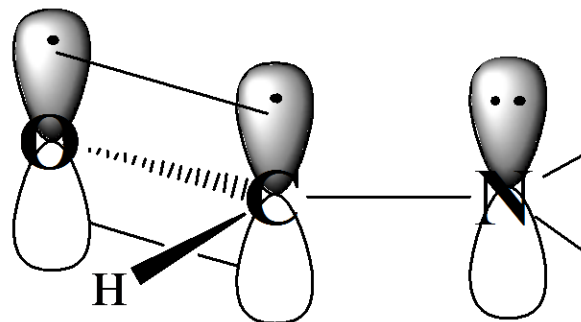
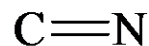
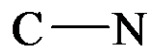
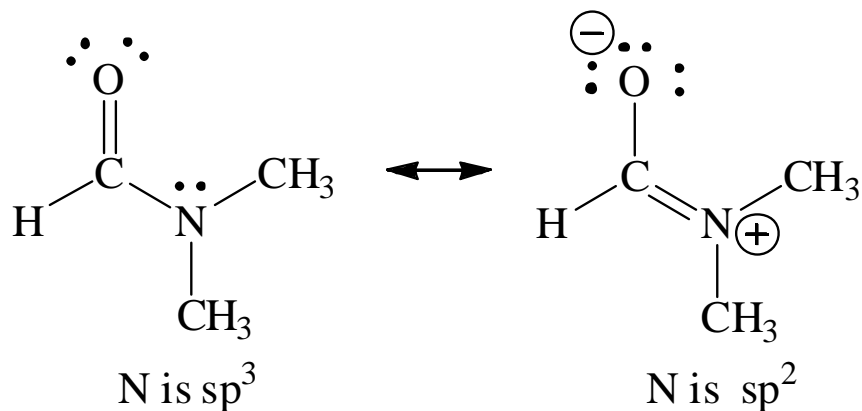


Carbene

Bonding

Hybridization and Resonance Structures

Frequently, different resonance structures predict different geometries about the same atom...



Remember: resonance structures show how electrons are delocalized, electrons are delocalized via π -bonds, π -bonds are formed by the overlap of atomic p orbitals. Since resonance structures do not permit the movement of atoms, the hybridization must be common throughout. This frequently occurs when a heteroatom is bonded to an sp² C.

Bonding – Molecular Orbital Theory

Molecular Orbital (MO) Theory Review – Chem 2000

- Since it is the valence electrons that 'do' the chemistry, we are usually most interested in the valence orbitals or molecules.
- We have looked at bonds as being the result of overlapping atomic orbitals and/or hybridized orbitals. We use the valence orbitals of the atoms in a given molecule to derive a set of new orbitals for the entire molecule. (Linear Combination of Atomic Orbitals (LCAO))

The principles:

- the number of molecular orbitals in a molecule must equal the number of valence atomic orbitals of the constituent atoms
- like all orbitals, MOs can hold two electrons at most.
- MOs can be delocalized - where atomic orbitals are found around an atom, molecular orbitals can be spread over the entire molecule
- MOs can be σ or π
- molecular orbitals can be bonding, non-bonding or anti-bonding
- a chart showing the relative energies of the MOs to each other and to the AOs from which they are derived is known as an MO diagram.

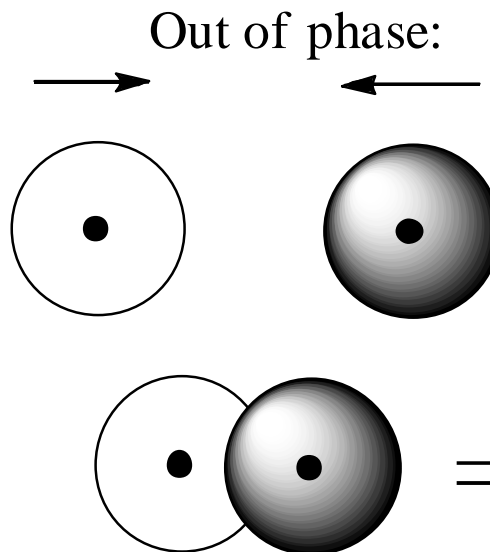
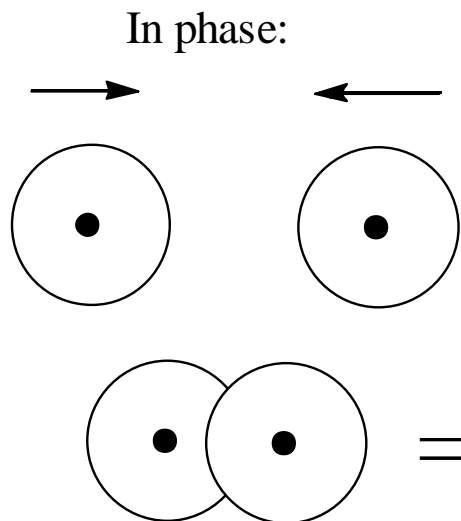
Bonding – Molecular Orbital Theory

To construct a valence molecular orbital diagram:

- Ignore the core electrons
- Total number of MOs = Total number of AOs
- Only AOs of **similar energy** combine to make LCAO-MOs

Bonding – Molecular Orbital Theory

Consider the H_2 molecule: we have ...



Bonding – Molecular Orbital Theory

- AOs describe the probability of finding an electron in a given region for an atom.
- MOs describe the probability of finding an electron in a given region for a molecule.
- MOs are spread across multiple atoms within the same molecule.
- AOs are labelled $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, etc. where the letters s , p , d , indicate the orbital shape.
- MOs are labelled 1σ , 2σ , 1π , 2π , etc. where the Greek letters σ or π , indicates the orbital symmetry.

Bonding – Frontier Molecular Orbitals

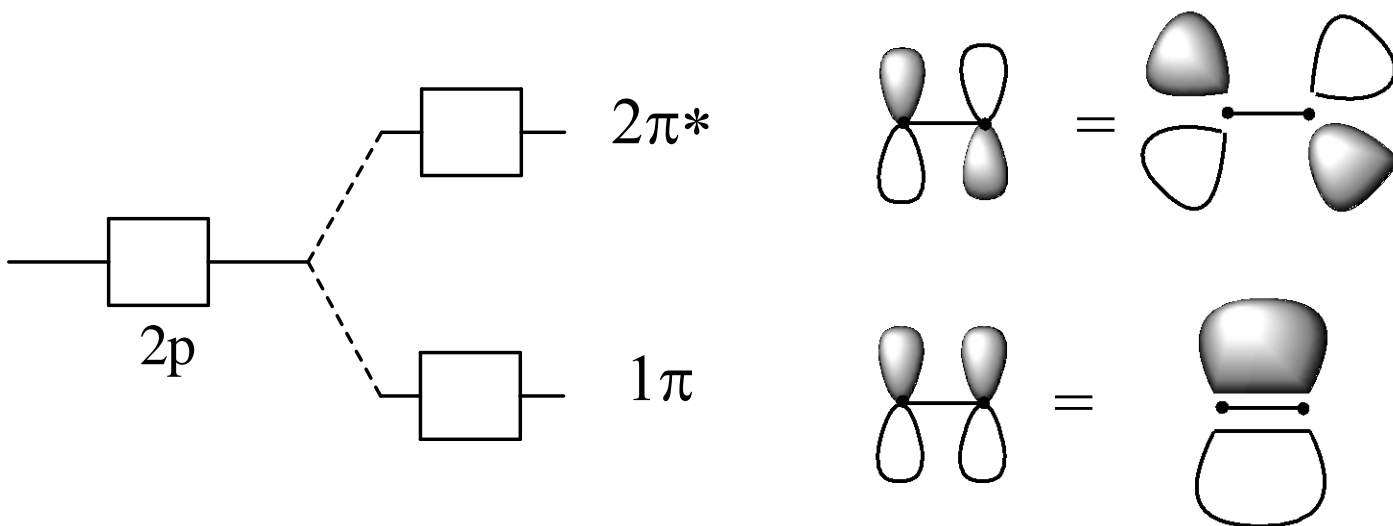
- The valence molecular orbitals (and not the core molecular orbitals) are the ones involved in reactions.
 - The most easily removed electrons from a molecule are in the **HOMO** (Highest Occupied Molecular Orbital).
 - The orbital which can most easily accept electrons is the **LUMO** (Lowest Unoccupied Molecular Orbital).
 - A **SOMO** (Singly Occupied Molecular Orbital) fills both roles.
- The HOMO, LUMO (and SOMO) are collectively referred to as the frontier molecular orbitals.

Bonding – Frontier Molecular Orbitals

- Recall the usual energy ranking for MOs (high to low):
 - sigma antibonding (σ^*)
 - pi antibonding (π^*)
 - nonbonding (lone pairs; can be σ or π)
 - pi bonding (π)
 - sigma bonding (σ)
- In molecules containing π bonds, the frontier orbitals tend to have π symmetry. In these molecules, the filled σ MOs tend to have much lower energy than the HOMO while the empty σ^* MOs tend to have much higher energy than the LUMO. As such, we often draw simplified MO diagrams that just show the π -symmetric MOs.
- THIS DOES NOT MEAN WE SHOULD FORGET LONE PAIRS!!! NOT EVEN THE ONES IN σ -SYMMETRIC MOs.

Bonding – π Molecular Orbital Diagrams

Ethylene:



Bonding – π Molecular Orbital Diagrams

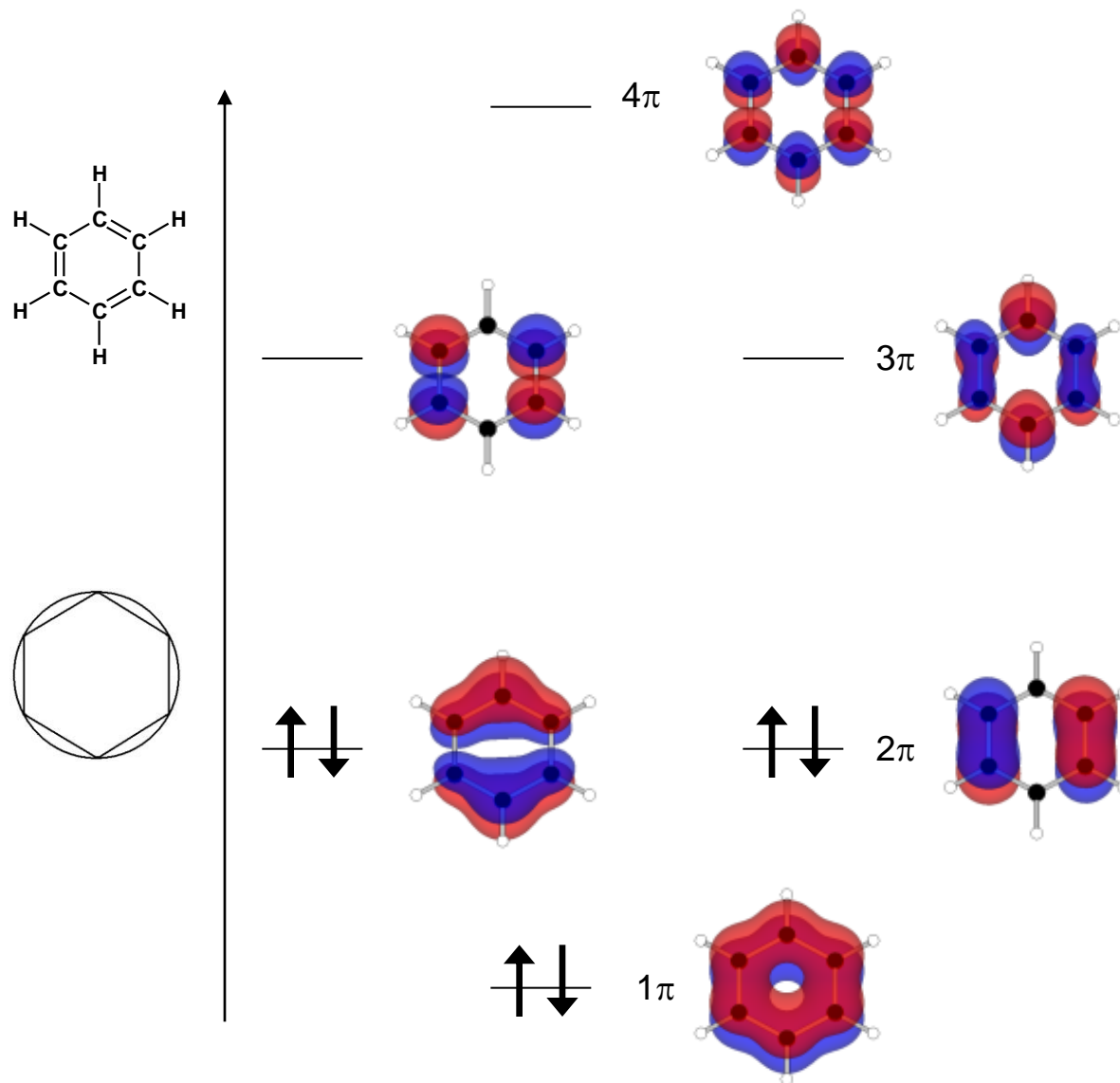
- The number of π -MOs is equal to the number of p orbitals which combined to make them.
- In a linear π -system, # energy levels = # π -Mos.
- # of delocalized π -electrons is equal to 2 electrons per double bond + 2 electrons per **lone pair that is part of the π -system.**

Bonding – π Molecular Orbital Diagrams

- The lowest energy π -MO has all p orbitals aligned in phase, with 0 nodes perpendicular to the plane of the π -system.
- The next π -MO will have 1 node perpendicular to the plane of the π -system
- The next π -MO will have two such nodes, etc.
- The highest energy π -MO will have every p orbital out-of-phase with the p orbitals on neighbouring atoms.

Bonding – π Molecular Orbital Diagrams

Benzene:



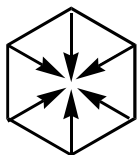
Benzene – Aromaticity

The Story of Benzene

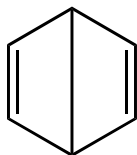
- first isolated from coal tar; formula found to be C_6H_6 .
- forms three dibromides, formulae $C_6H_4Br_2$
- undergoes substitution reactions rather than addition reactions.

The structure problem: 4 units of unsaturation yet this molecule did not behave like an alkene or alkyne. Indeed, benzene is much less reactive and more stable than might be expected.

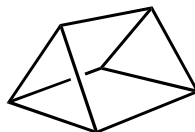
There were several proposed structures put forward at the time (mid 1800s):



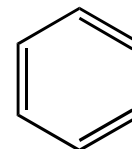
Klaus



Dewar benzene

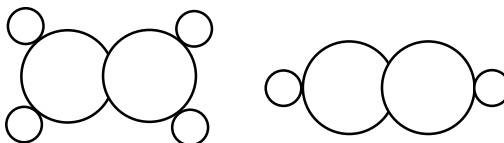
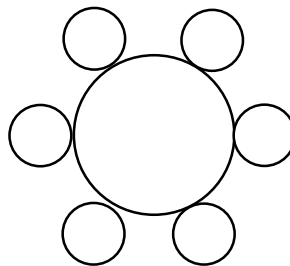


Now known as
Prismane.



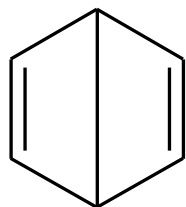
The Kekulé
structure - 1865

Joseph Loschmidt - 1861

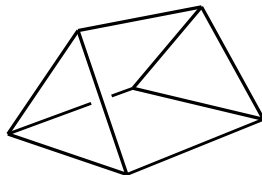


Benzene – Aromaticity

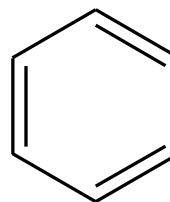
Only three dibromobenzenes...



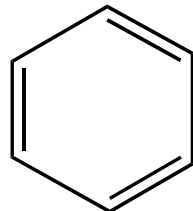
Dewar benzene



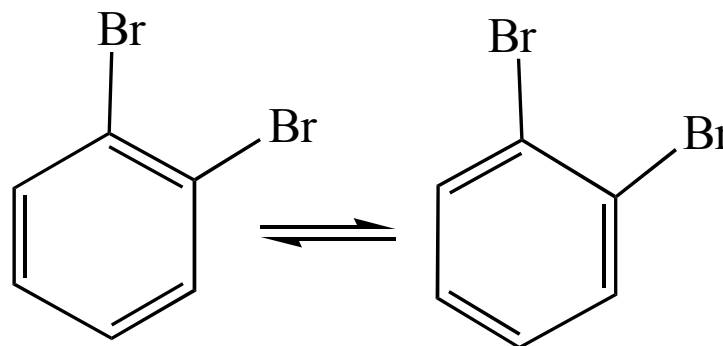
Now known as Prismane.



The Kekulé structure - 1865



1,3,5-Cyclohexatriene
(drawn to scale)

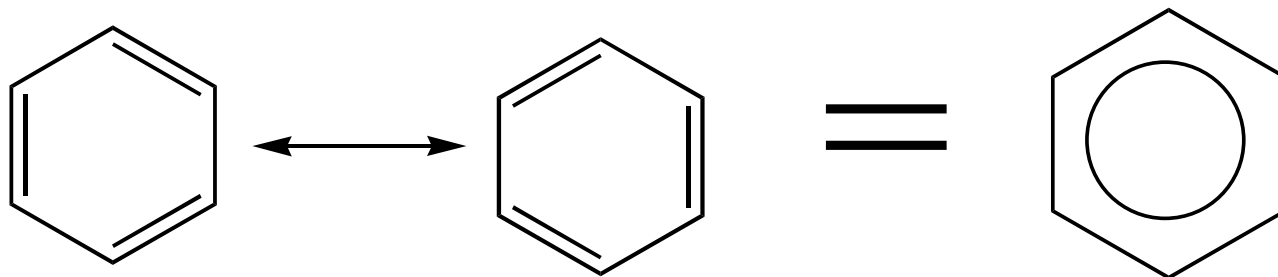


Kekulé's proposal:

- All six carbon-carbon bonds are the same length: 1.40\AA . This is intermediate between the single C-C and double C=C bond length suggested by the hypothetical molecule 1,3,5-cyclohexatriene.

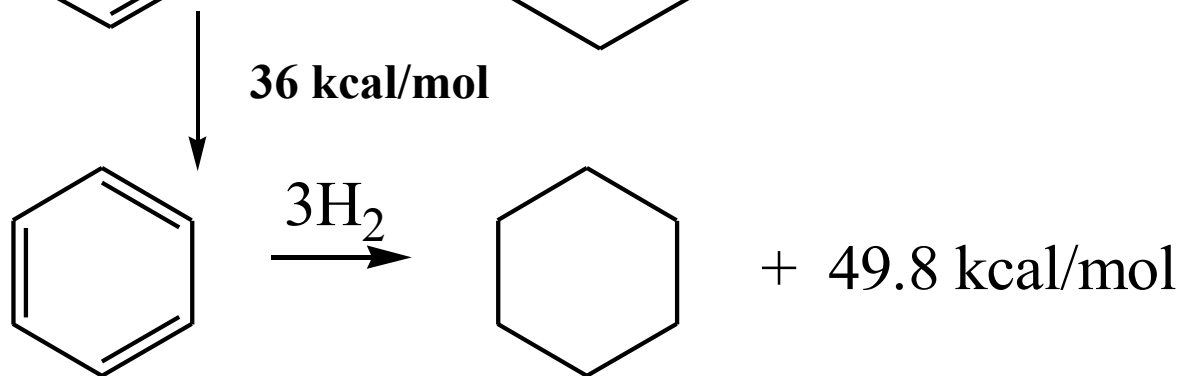
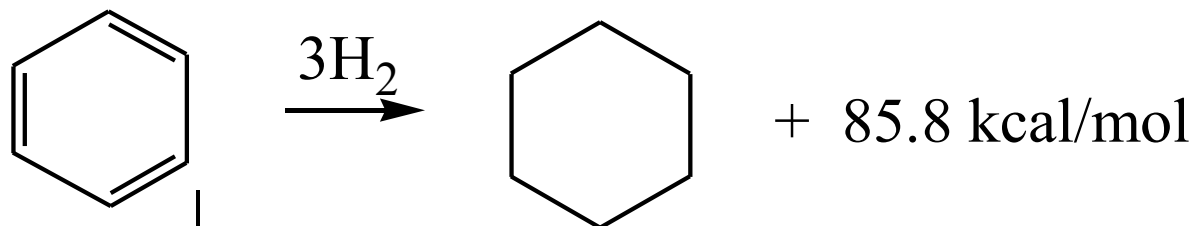
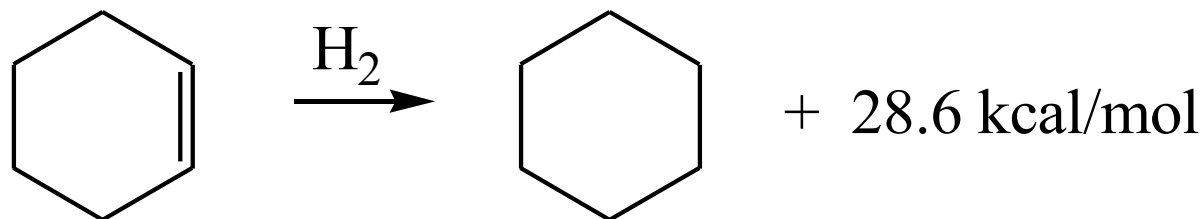
Benzene – Aromaticity

Now we understand more about electron delocalization...



Benzene – Aromaticity

- The unusual stability of benzene...



36 kcal/mol

- The addition of H_2 to a double bond is usually exothermic.

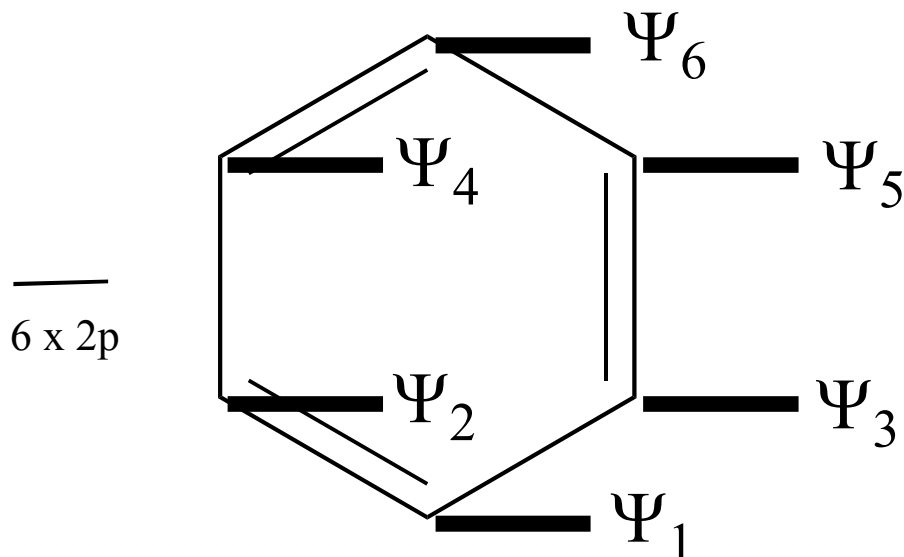
- Benzene is 36 kcal/mol more stable than the non-delocalized cyclohexatriene. We call this ...

Resonance Energy

Benzene – Aromaticity

Why the extra stability?

The π -MO Diagram of Benzene:



- The stability of benzene can be attributed to the set of filled bonding π -type molecular orbitals that result from the atomic p-orbitals around the ring.. Benzene has a filled set of low-energy π -molecular orbitals, just as the Noble Gases have a filled set of atomic orbitals. Molecules that share this kind of stability are said to be...

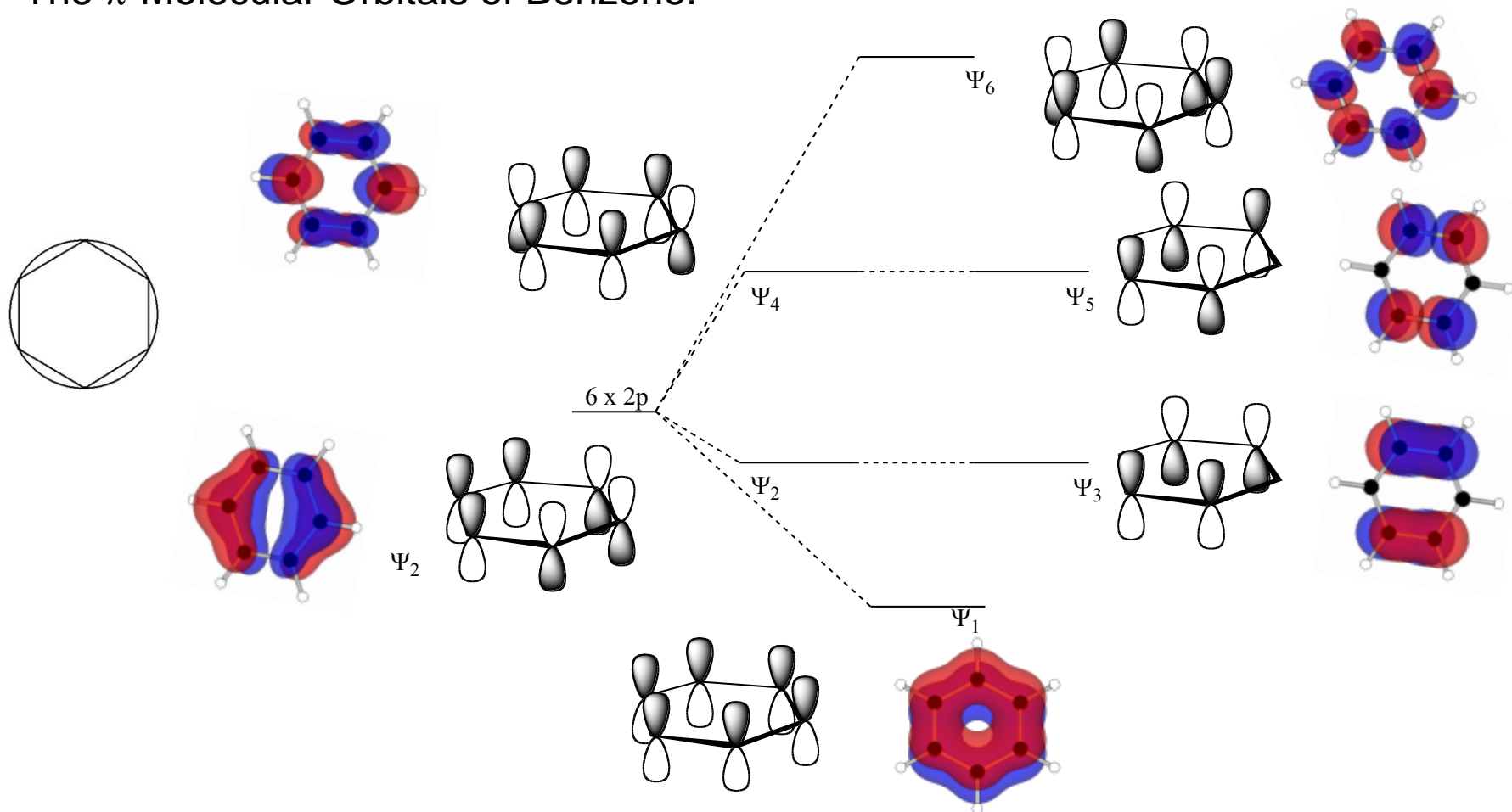
Aromatic

Benzene – Aromaticity

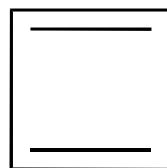
Originally, this had to do with their smell, but now the term aromatic is used to refer to compounds which have electrons that are delocalized around the ring.

Aromatic molecules exhibit a ring current due to the delocalization of their π -electrons which can be observed...

The π -Molecular Orbitals of Benzene:

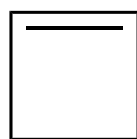


Antiaromaticity



Cyclobutadiene

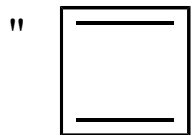
4 π -electrons



+ H₂



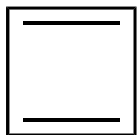
-41.6 kcal/mol



+ 2 H₂



-83.2 kcal/mol



+ 2 H₂

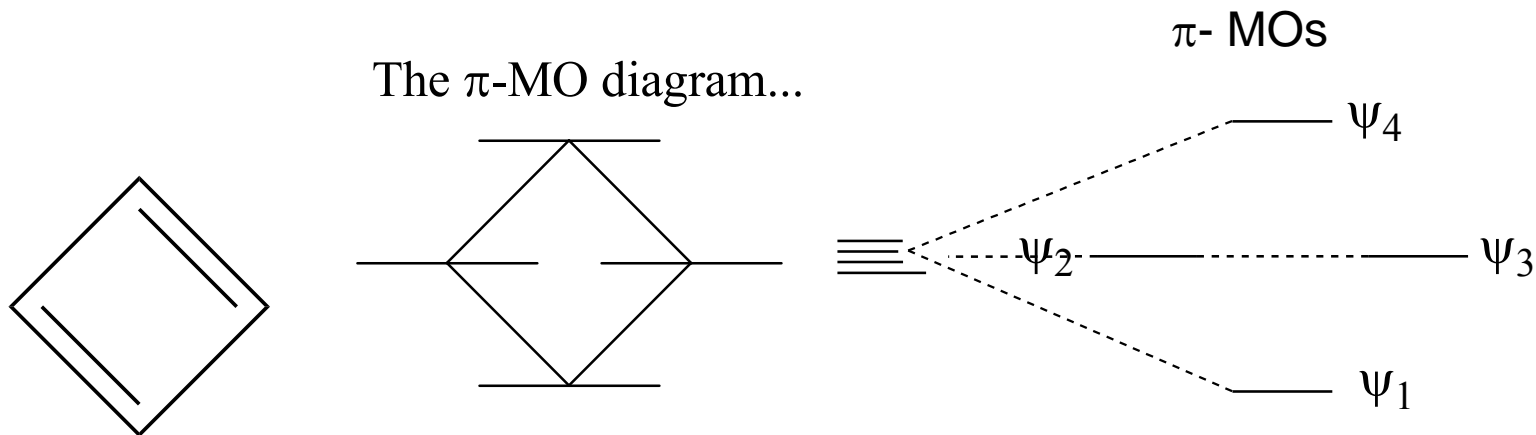


-101.9 kcal/mol

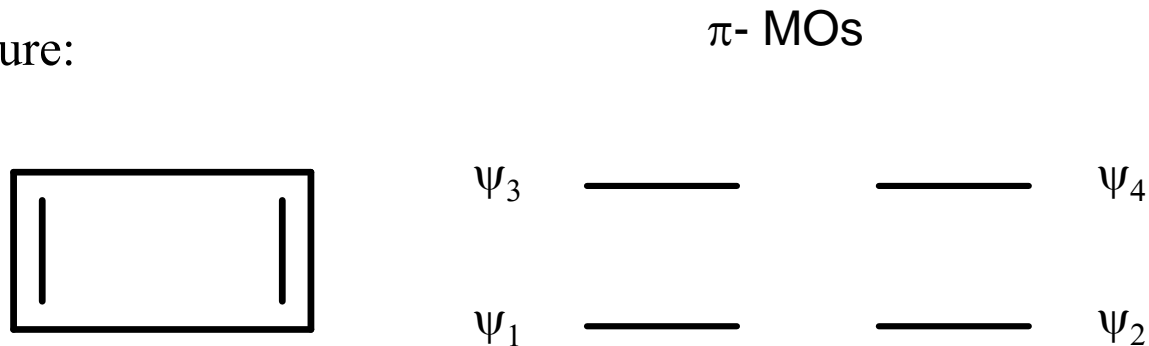
!

So, the resonance energy of cyclobutadiene is... -18.7 kcal/mol

Antiaromaticity



The actual structure:



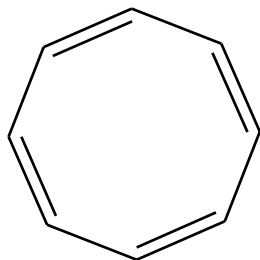
- Molecules whose π MO diagrams predict them to be diradicals are less stable than the bond-localized alkenes, have negative resonance energies and are said to be...

Anti-aromatic.

Antiaromaticity

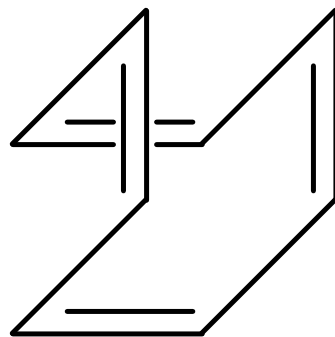
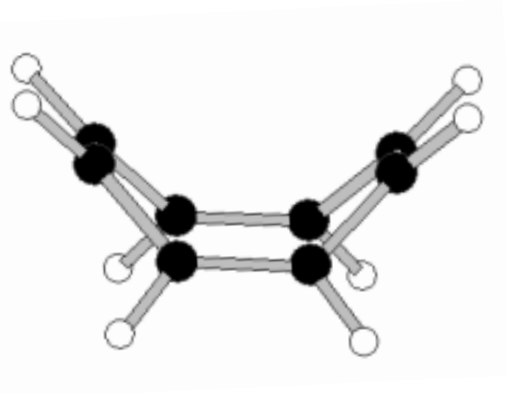
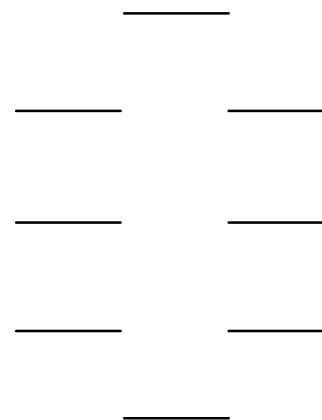
- Sketch a π MO diagram for the cyclopropenyl cation and anion. For the two ions, indicate if it is aromatic, antiaromatic, or nonaromatic.

Aromaticity



1,3,5,7-Cyclooctatetraene
8 π -electrons

π -MOs

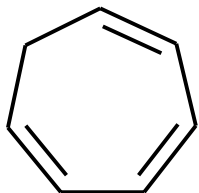


Molecules that do not have a continuous circuit of atomic p orbitals available for electron delocalization are...

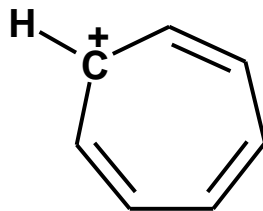
Non-aromatic.

Aromaticity

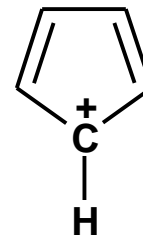
- Are the following compounds aromatic, antiaromatic or non-aromatic?



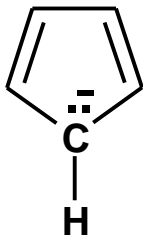
1,3,5-cycloheptatriene



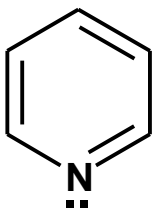
tropylium cation



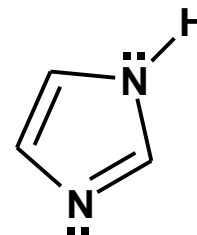
cyclopentadienyl cation



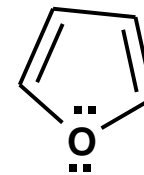
cyclopentadienyl anion



pyridine



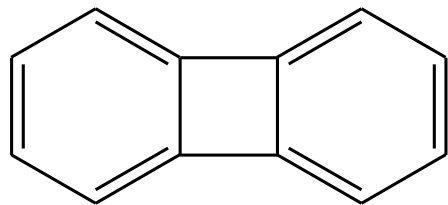
imidazole



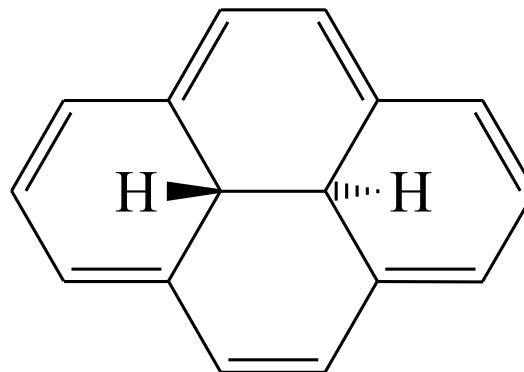
furan

Aromaticity

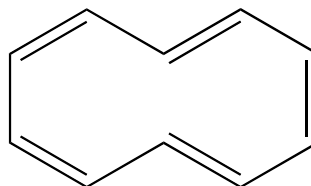
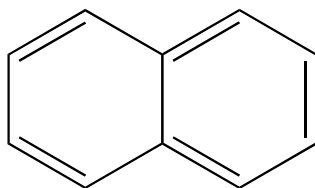
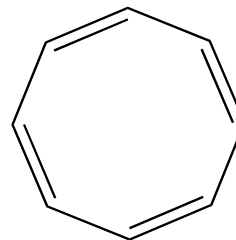
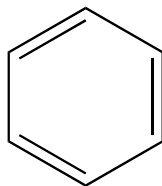
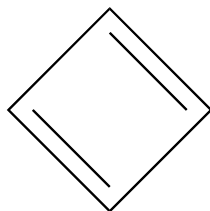
- Are the following compounds aromatic, antiaromatic or non-aromatic?



Biphenylene
12 π -electrons



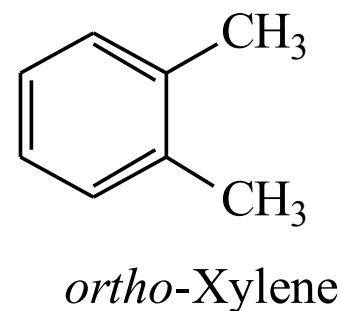
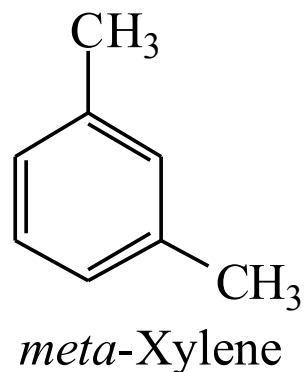
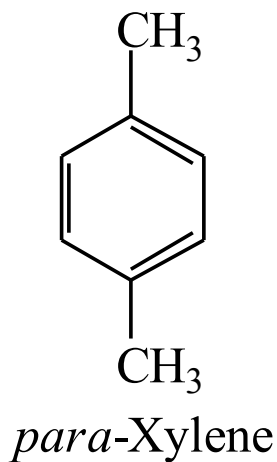
Dihydropyrene
14 π -electrons



Nomenclature of Aromatic Compounds

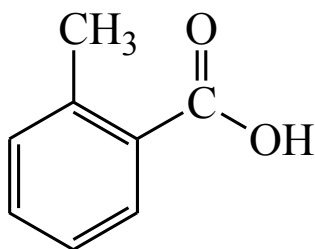
Substituted Benzenes

In disubstituted benzenes, the relative positions of the two substituents must be specified. There are two ways in which this is done. IUPAC uses a numbering system. A trivial method also persists.

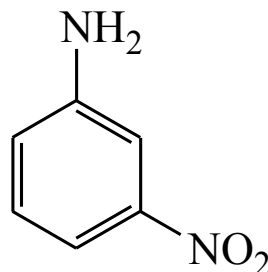


Aromaticity

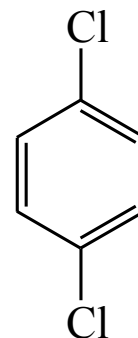
Polysubstituted Benzenes are named as derivatives of the parent benzene (if applicable). Substituent positions are numbered from the dominant functional group, or follow rules akin to those for numbering alkanes.



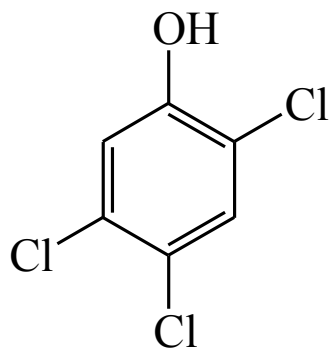
o-Methylbenzoic acid
(2-Methylbenzoic acid)



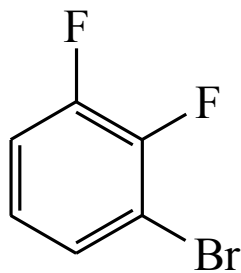
m-Nitroaniline
(3-Nitroaniline)



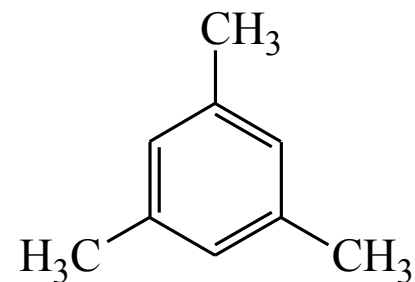
p-Dichlorobenzene
(1,4-Dichlorobenzene)



2,4,5-Trichlorophenol



1-Bromo-2,3-difluorobenzene



1,3,5-Trimethylbenzene
(Mesitylene)