NATURE OF BONDING IN ORGANIC MOLECULES (P.G. SEM-1, CC-III)

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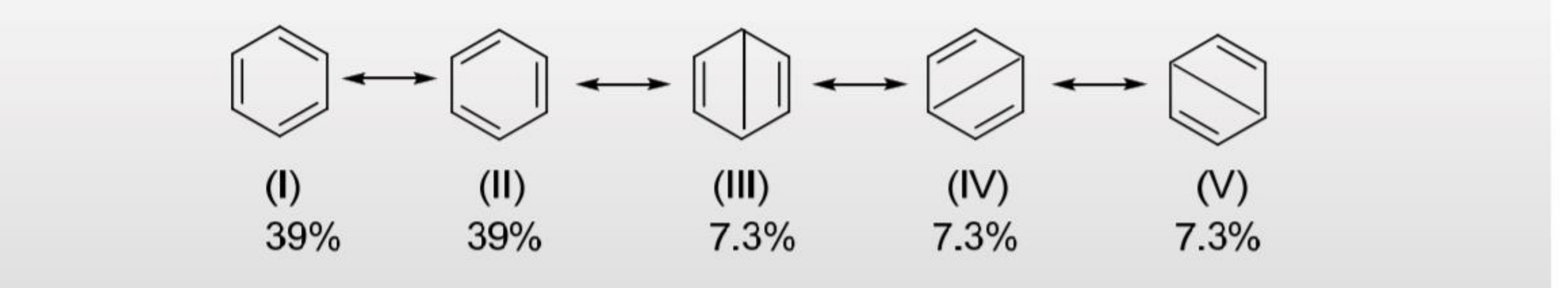
ARRAH

DELOCALISED CHEMICAL BONDING

DELOCALIZED CHEMICAL BONDING MAY BE DEFINED AS BONDING IN WHICH THE ELECTRONS ARE SHARED BY MORE THAN TWO NUCLEI. DELOCALIZED ELECTRONS ARE CONTAINED WITHIN AN ORBITAL THAT EXTENDS SEVERAL ADJACENT ATOMS. IN VALENCE BOND THEORY, DELOCALIZATION IN BENZENE IS REPRESENTED BY RESONANCE STRUCTURES.

GENERAL DESCRIPTION

- A. The valence-bond method ☐ resonance concept (Pauling, 1928) Several possible Lewis structures are drawn and the molecule is taken to be a weighted average of them. This representation of a real structure structure as a weighted weighted average average of two or more canonical canonical forms is called resonance



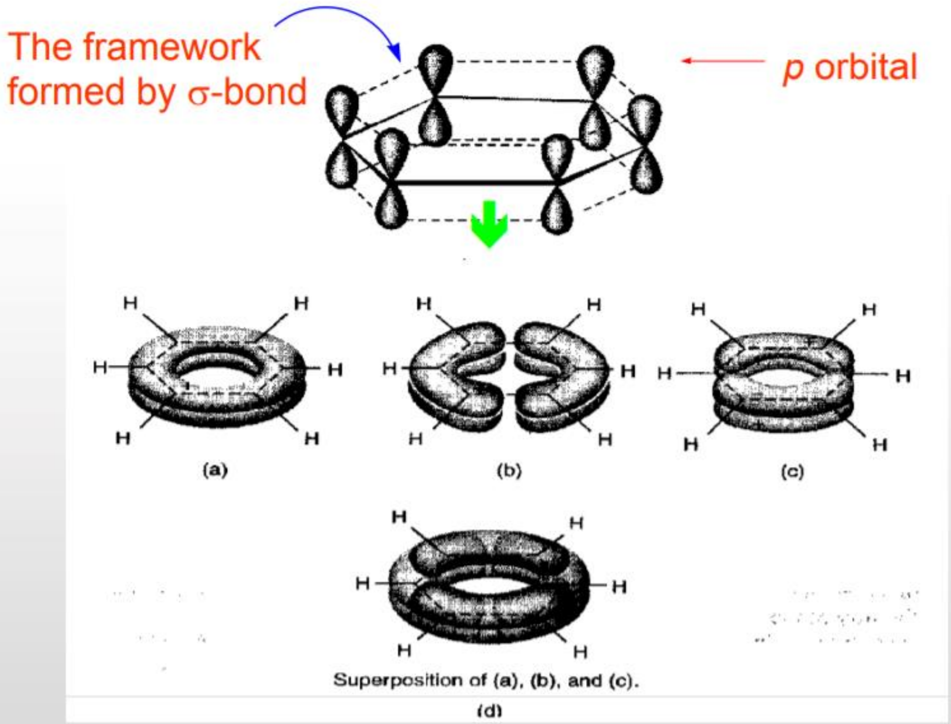
The different different structures structures contributing contributing to the resonance resonance hybrid are referred referred to as CANONICAL FORMS of the molecule. The more stable a canonical form, the more it contributes to the RESONANCE HYBRID

TRUE NATURE OF RESONANCE

- When a molecule cannot be represented by the standard tools of valence bond theory (promotion, hybridisation, orbital overlap, sigma and ☐ bond formation) because no single strtucture predicted by VB can account for all the properties of the molecule, one invokes the concept of resonance.
- The bond order of a particular particular bond is the sum of the weights weights of those canonical forms in which the bonds is double plus 1 for the single bond that is present in all of them.
- ■ The C-C bond order of C bond order of benzene = 1.463 The magnitude of the bond order is associated with the bond length. (0.39+0.073+1) g According to Pauling, the bond order is experimentally described by:
- Sij=e^(Rij+dij)/b
- Where Rij is the bond length experimentally measured, dij is the single bond length, and b is a constant, depending on the atoms. A good approximation

B. THE MOLECULAR-ORBITAL METHOD ☐

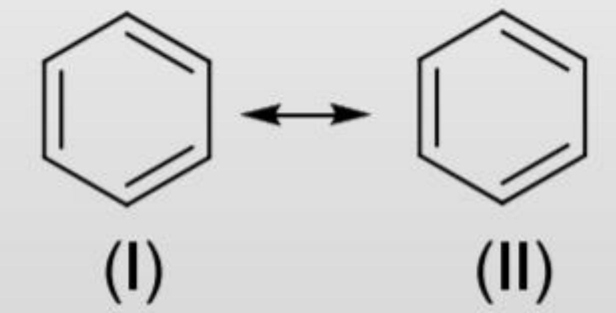
- Hückel molecular-orbital (HMO) Method (1931) For planar unsaturated unsaturated and aromatic aromatic molecules molecules, many molecular molecular - orbital calculations (MO calculations) have been made by treating the ☐ and ☐ electrons electrons separately separately. It is assumed assumed that the orbitals orbitals can be treated as localized bonds and the calculations involve only the ☐ electrons.
- Hückel molecular orbital method (HMO): a very simple linear combination o f atomic orbitals to molecula r orbitals (LCAO MO) method for the determination of energies of molecular orbitals of ☐ electrons in conjugated hydrocarbon systems, such as ethylene, benzene and butadiene.



The six *p* orbitals of benzene overlap to form three bonding orbitals, (a), (b), and (c). (d) is the superimposed three orbitals.

BOND ENERGIES ENERGIES AND DISTANCES IN COMPOUNDS CONTAINING DELOCALIZED BONDS

- Resonance hybrids are always more stable than any of the canonical structures would be, if they existed. The delocalization of the electrons lowers the orbital energies, energies, imparting this stability. The gain in stability of the resonance hybrid over the most stable of the (non-existent) canonical structures is called the RESONANCE ENERGY or DELOCALISATION ENERGY.
- Estimation of resonance energy from
- the heat of atomization
- the heat of hydrogenation
- HMO theory



The most stable canonical structures of benzene

- Resonance energy from the heat of hydrogenation:

	the heat of hydrogenation (kJ/mol)
cyclohexene:	120
the hypothetical (I) or (II):	360
the real benzene:	208
the resonance energy:	152 kJ/mol

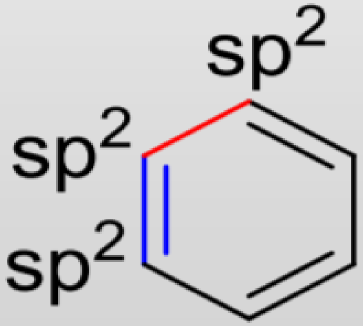
NOTE: One must bear in mind again that resonance structures have no physical existence. So, even though the term 'resonance energy' is quite meaningless, it offers an insight into how different the VB picture of a molecule is from the actual molecule itself.

Bond length

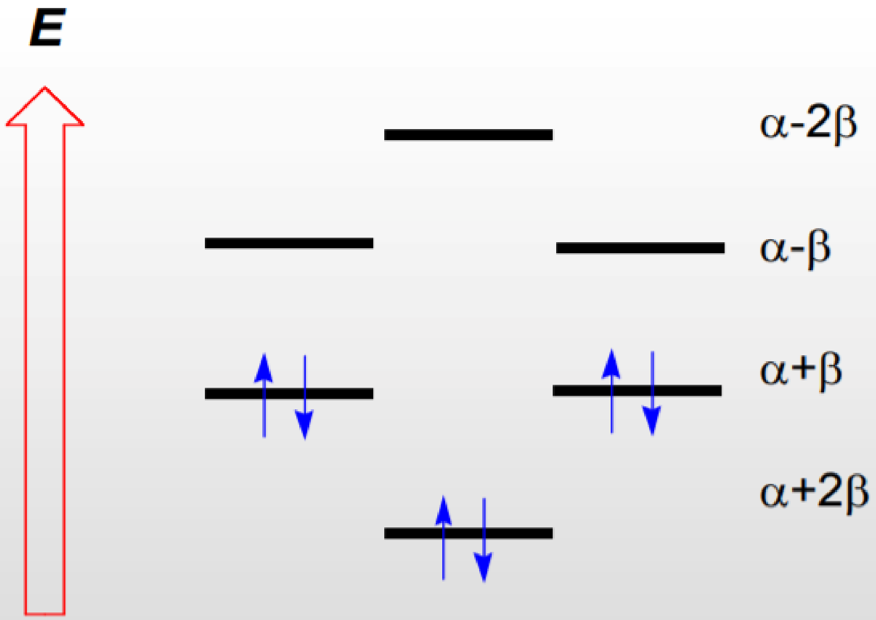
sp^2-*sp*^{2} C—C: 1.48 Å

sp^2-*sp*^{2} C=C: 1.32 Å

C-C bond distance in benzene: **1.40 Å**



- The energies of six benzene orbitals can be calculated from HMO theory in terms of two quantities, α and β.



α is the amount of possessed by an isolated 2*p* orbital before overlap

β (*resonance integral*) is an energy unit expressing the degree of stabilization resulting from π-orbital overlap

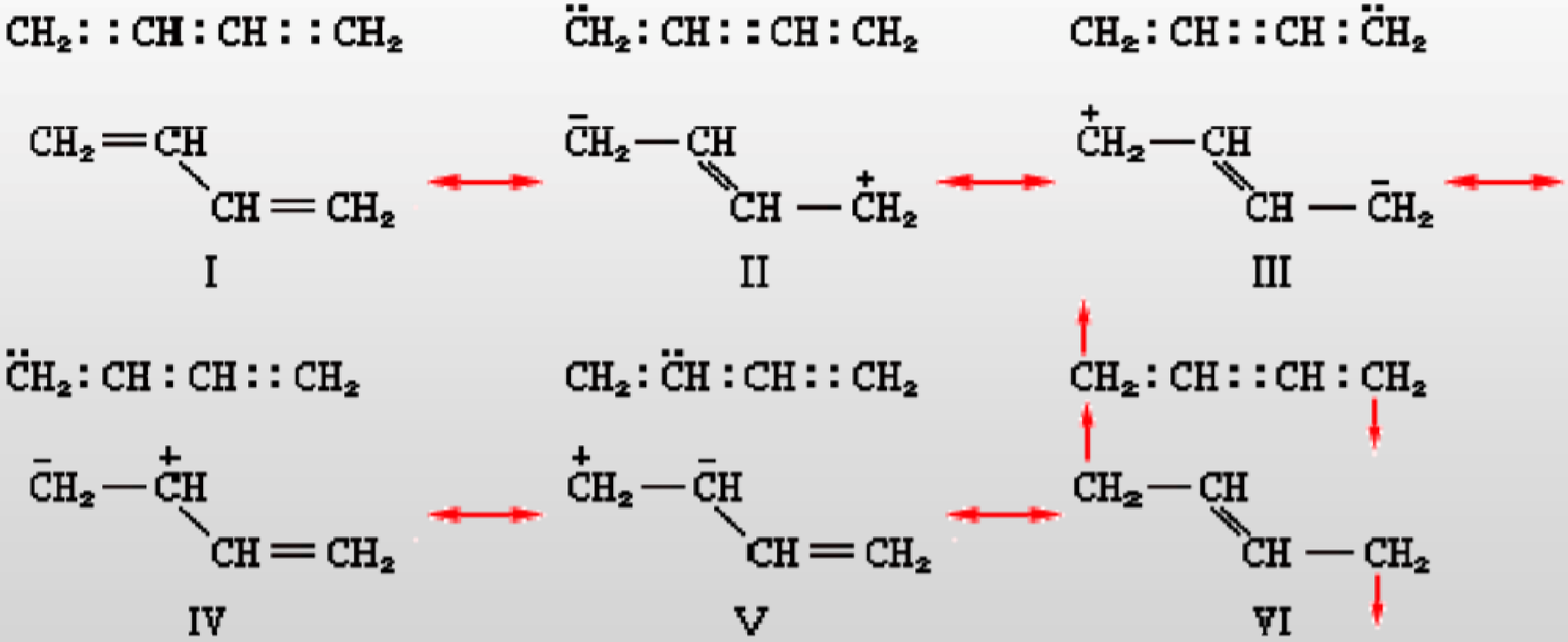
Energy level of benzene

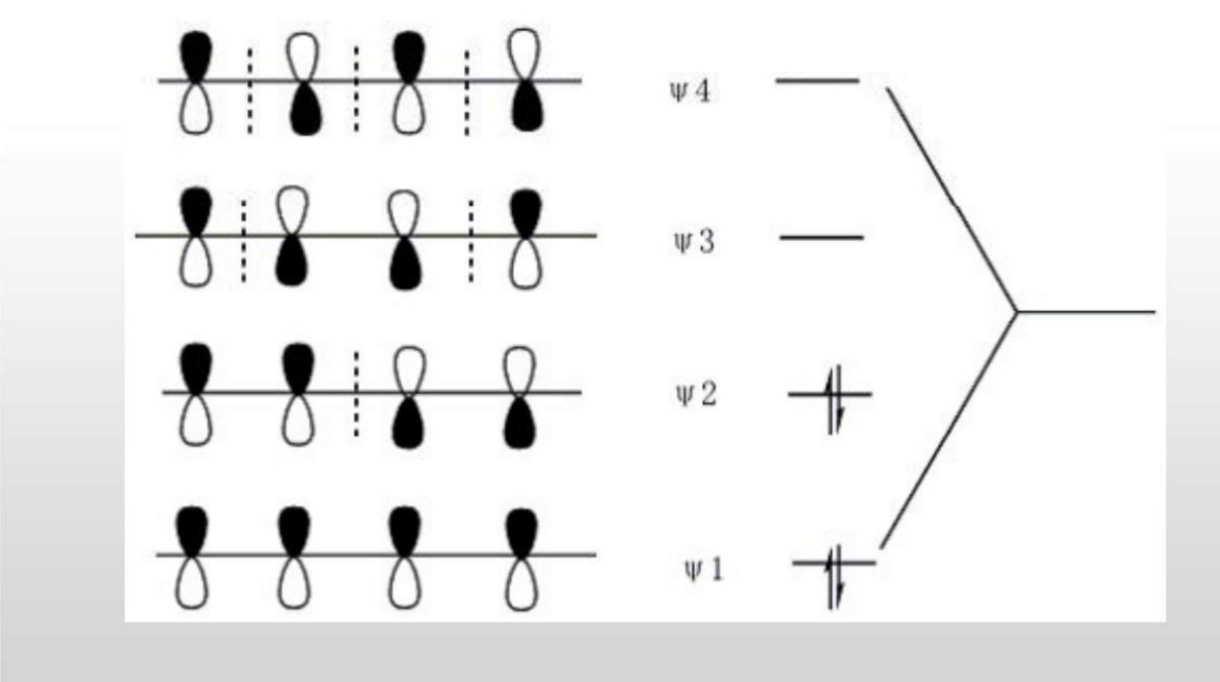
The resonance energy= $(6\alpha+8\beta)-(6\alpha+6\beta) = 2\beta$

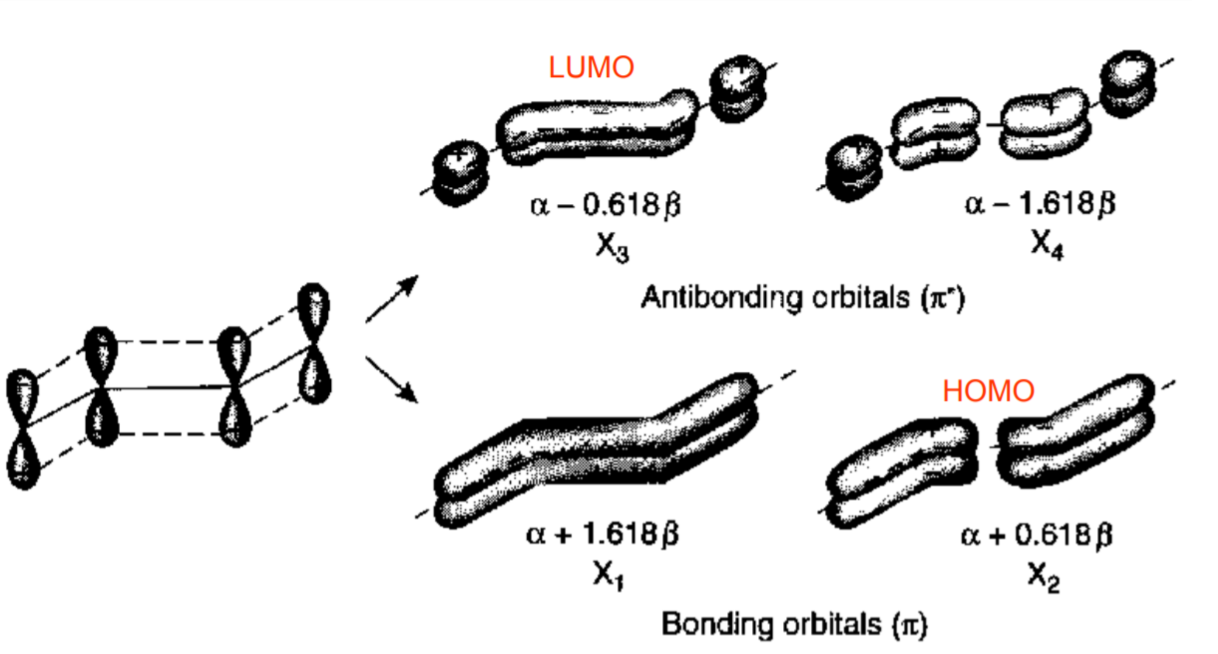
1.2.3 Kinds of molecules that have delocalized bonds

1.2.3.1 Double or triple bonds in conjugation

A system of atoms covalently bonded with alternating single and multiple bonds is a conjugated system.



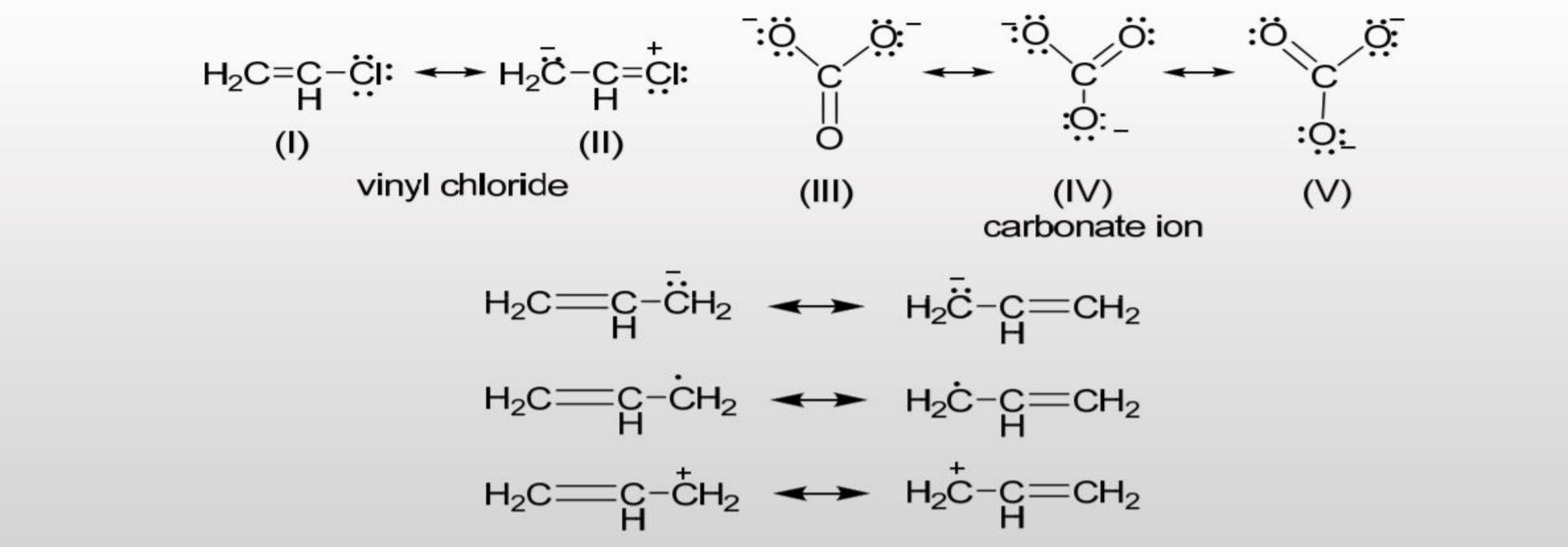

ψ4
ψ3
ψ2
ψ1

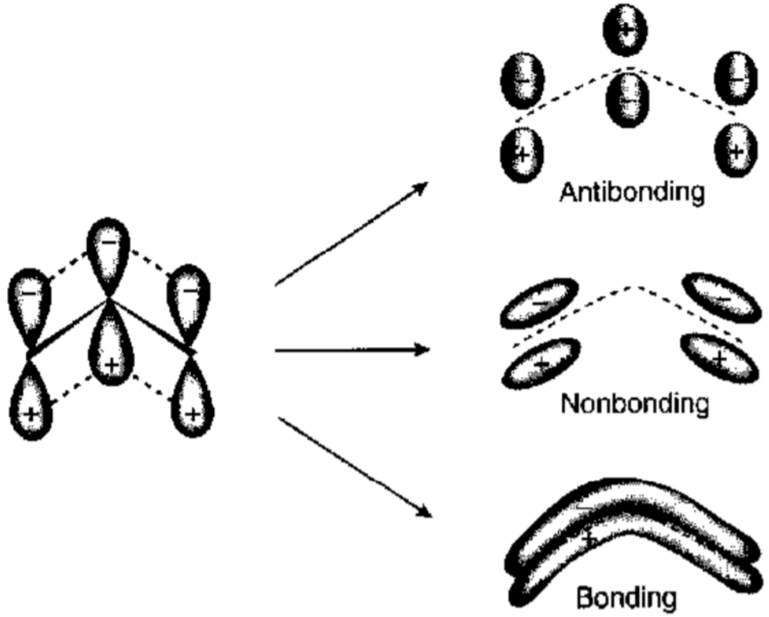


The four π orbitals of butadiene, formed by overlap of four *p* orbitals

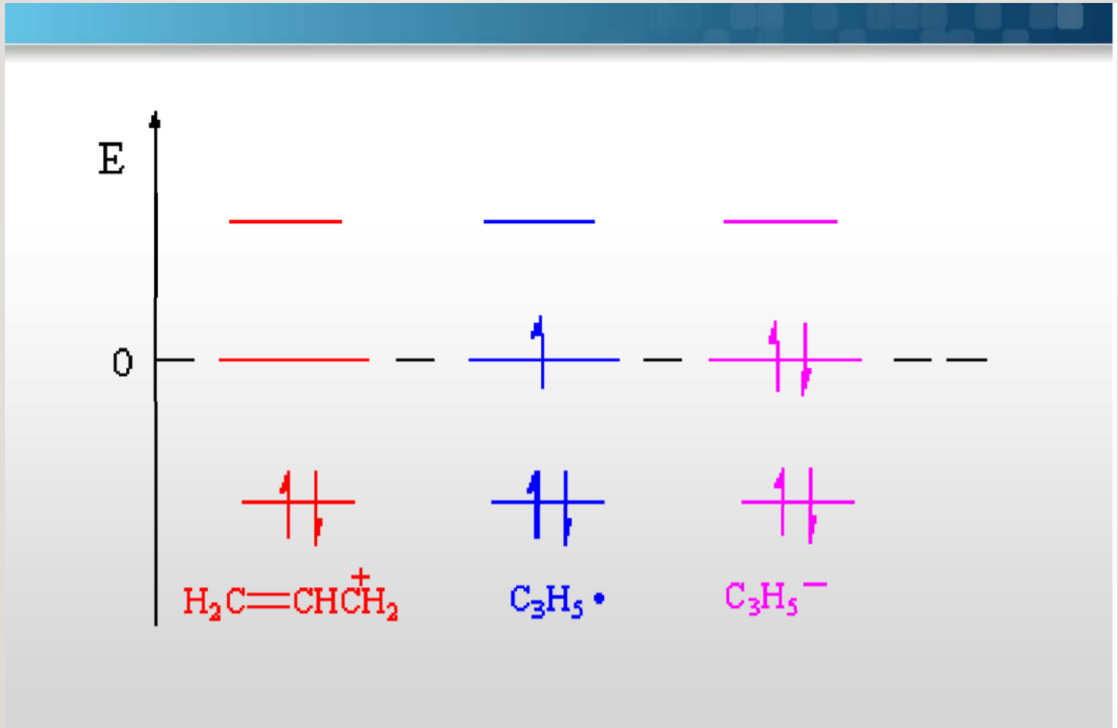
DOUBLE OR TRIPLE BONDS IN CONJUGATION WITH A P ORBITAL ON AN ADJACENT ATOM

- There are three cases: the original original p orbital orbital may have contained contained two, one, or no electrons electrons.



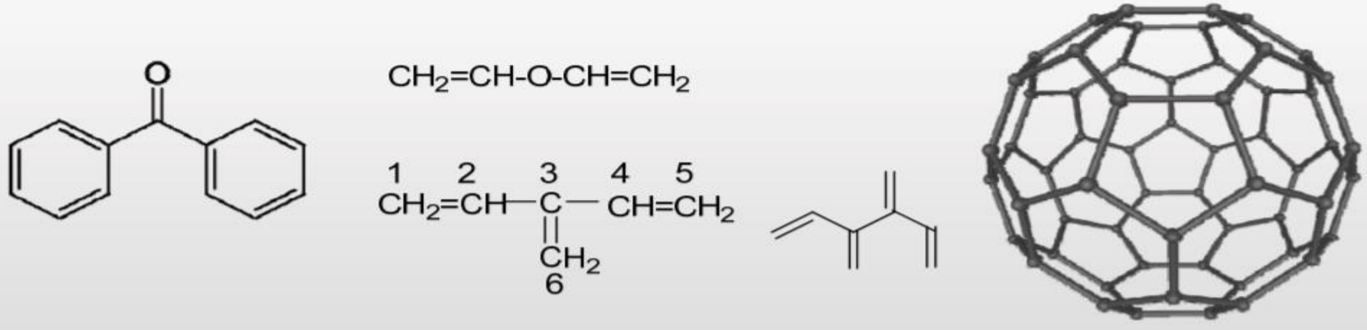


The three orbitals of an allylic system, formed by overlap of three *p* orbitals.


E
0
$H_2C{=}CH\overset{+}{C}H_2$
$C_3H_5\,\bullet$
$C_3H_5^{-}$

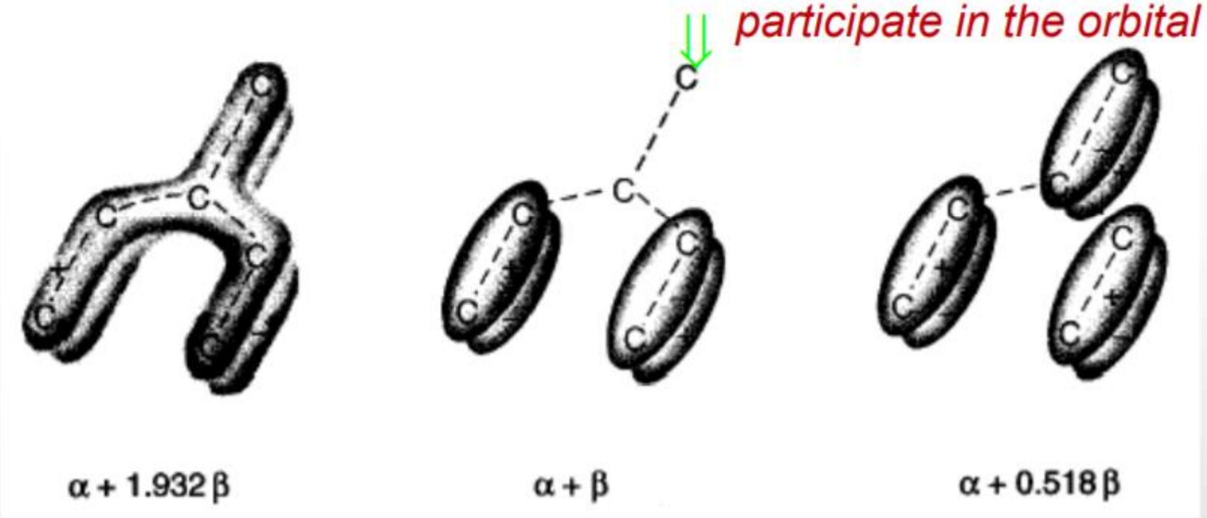
CROSS-CONJUGATION

- In a cross-conjugation compound, three groups are present, two of which are not conjugated with each other, although each is conj- ugated with the third. The type of conjugation has an impact on reactivity and molecular electronic transitions.



benzophenone, divinylether, dendralenes and Buckminsterfullerene C_{60}

MO treatment: 6 *p* orbitals ⇒ 6 molecular orbitals (3 bonding orbitals shown below)



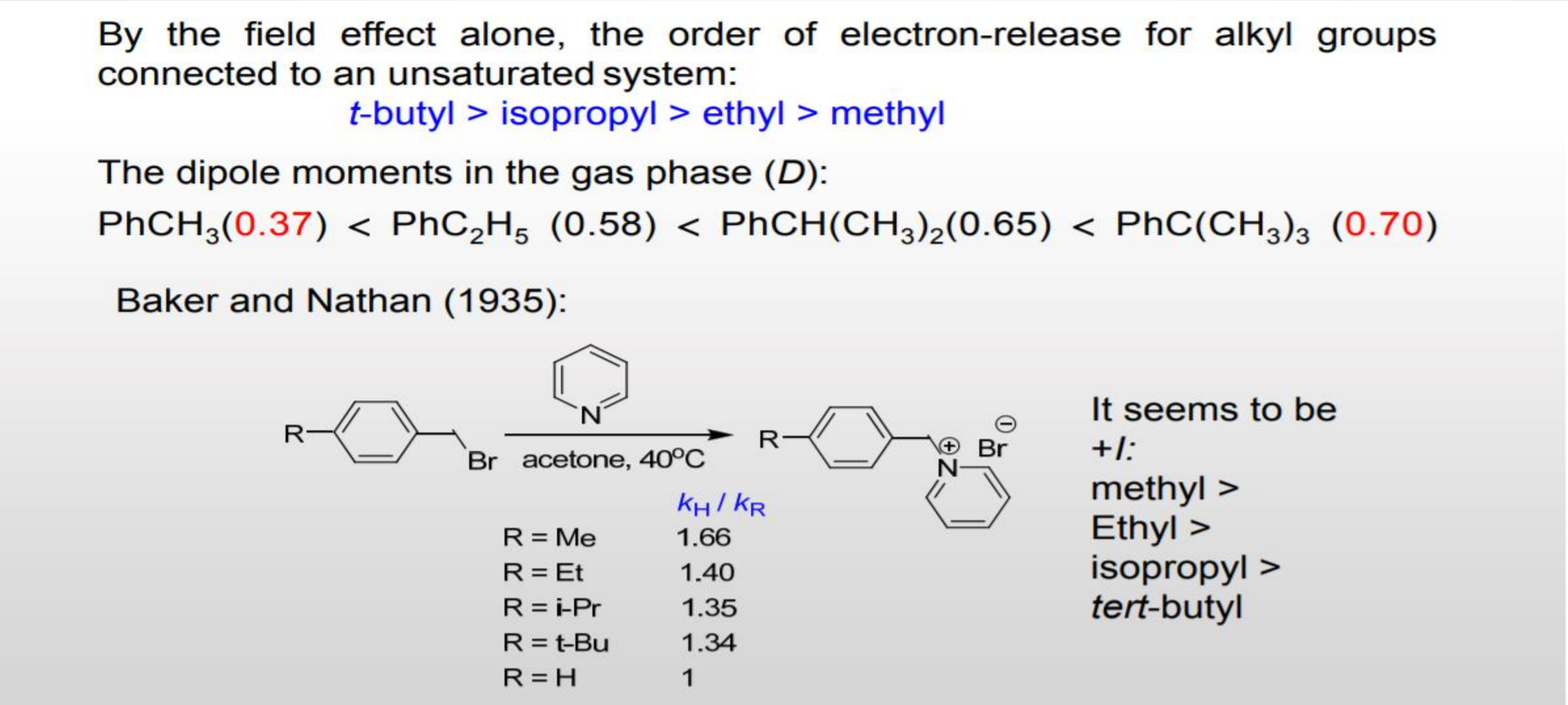
2 carbon atoms do not participate in the orbital

$\alpha + 1.932\beta$ $\alpha + \beta$ $\alpha + 0.518\beta$

The three bonding orbitals of 3-methylene-1,4-pentadiene

The total energy of the occupied orbitals = $6\alpha + 6.900\beta$
The resonance energy = $0.900\ \beta$

HYPERCONJUGATION



By the field effect alone, the order of electron-release for alkyl groups connected to an unsaturated system:

t-butyl > isopropyl > ethyl > methyl

The dipole moments in the gas phase (*D*):

$PhCH_3(0.37) < PhC_2H_5\ (0.58) < PhCH(CH_3)_2(0.65) < PhC(CH_3)_3\ (0.70)$

Baker and Nathan (1935):

	k_H / k_R
R = Me	1.66
R = Et	1.40
R = i-Pr	1.35
R = t-Bu	1.34
R = H	1

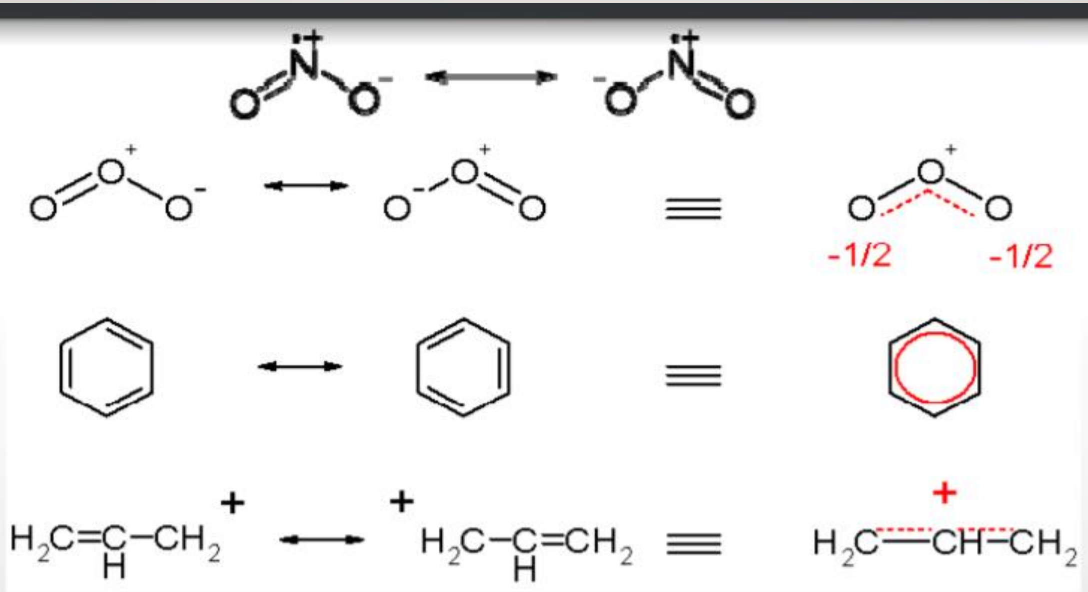
It seems to be
+*I:*
methyl >
Ethyl >
isopropyl >
tert-butyl

WHAT IS THE HYPERCONJUGATION?

- Hyperconjugation is the stabilizing interaction that results from the interaction interaction of the electrons electrons in a sigma bond (usually (usually C-H or C-C) with an adjacent empty (or partially filled) non-bonding p-orbital or antibonding pi orbital or filled pi orbital to give an extended molecular orbital that increases the stability of the system.

THE RULES OF RESONANCE

- ☐ We have seen that one way of expressing the actual structure of a molecule containing delocalized bonds is to draw several possible structures and to assume that the actual molecule is a hybrid of them. These canonical forms have no existence except in our imaginations. The molecule does not rapidly shift between them. It is not the case that some molecules have one canonical form and some another. All the molecules of the substance have the same structure. That structure is always the same all the time and is a weighted average of all the canonical forms.
- 1. All the canonical forms must be bona fide Lewis structures. For instance, none of them may have a carbon with five bonds.
- 2. The positions of the nuclei must be the same in all the structures. This means that all we are doing when we draw the various canonical forms is putting the electrons in different ways.



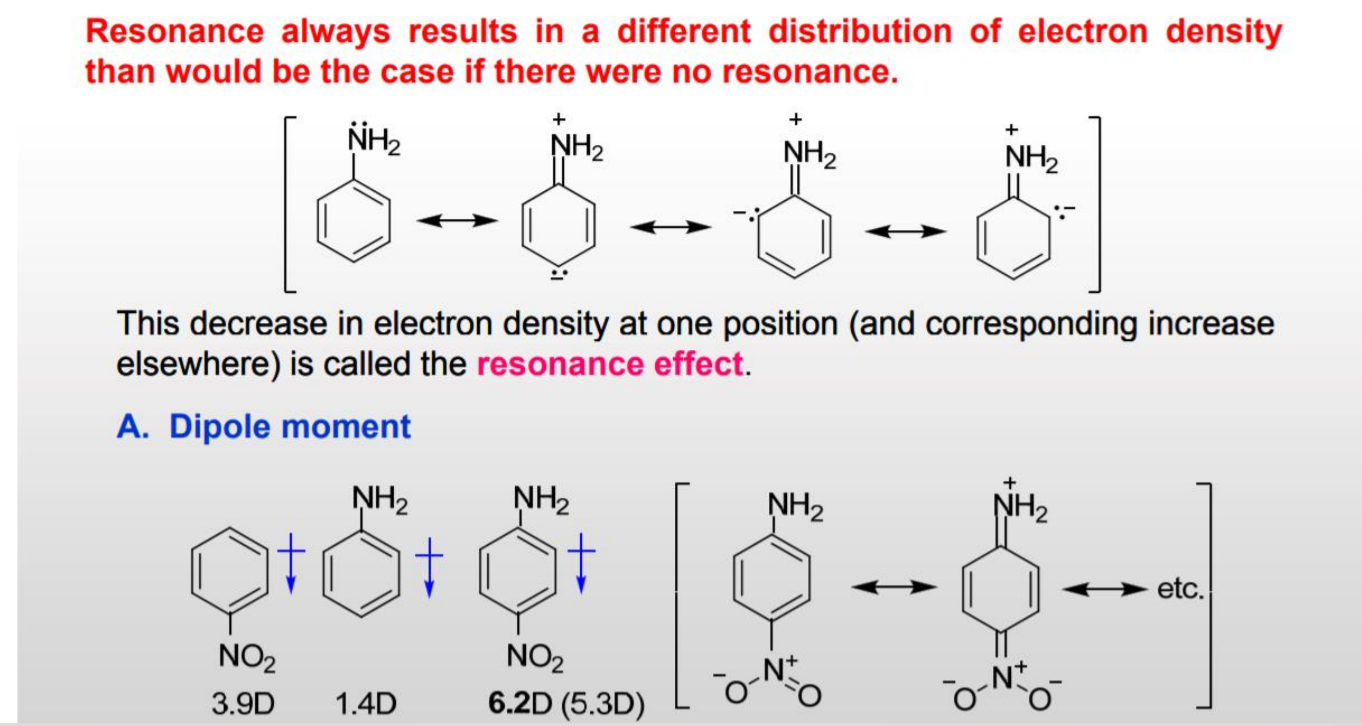
Examples of resonance –nitrogen dioxide, ozone, benzene and allyl cation.

Note: In most resonance, σ bonds are not involved, and only the π or unshared electrons are put in different ways. This means that if we write one canonical form for a molecule, we can then write the others by merely moving π and unshared electrons.

- 3. All atoms taking part in the resonance, resonance, i.e., covered by delocalized electrons, electrons, must lie in a plane or nearly so. This, of course, course, does not apply to atoms that have the same bonding in all the canonical forms. The reason for planarity is maximum overlap of the p orbitals.
- 4. All canonical forms must have the same number of unpaired electrons.
- 5. The energy of the actual molecule is lower than that of any canonical form, obviously. Therefore, delocalization is a stabilizing phenomenon.
- 6. All canonical forms do not contribute equally to the true molecule. Each form contributes in proportion to its stability, the most stable form contributing most.

- The greater the number of significant structures that can be written and the more nearly equal they are, the greater the resonance energy, other things being equal. The helpful rules for deciding relative stabilities of imaginary structures :
- a. Structures with more covalent bonds are ordinarily more stable than those with fewer.
- b. Stability is decreased by an increase in charge separation. Structures with formal charges are less stable than uncharged structures.
- c. obeying as much as possible the octet rule (8 valence electrons around each atom rather than having deficiencies or surplus). Structures that carry a negative charge on a more electronegative atom are more stable than those in which the charge is on a less electronegative atom. Similarly, Similarly, positive charges are best carried on atoms of low elctronegativity.
- d. Structures with distorted bond angles or lengths are unstable, unstable.

THE RESONANCE EFFECT

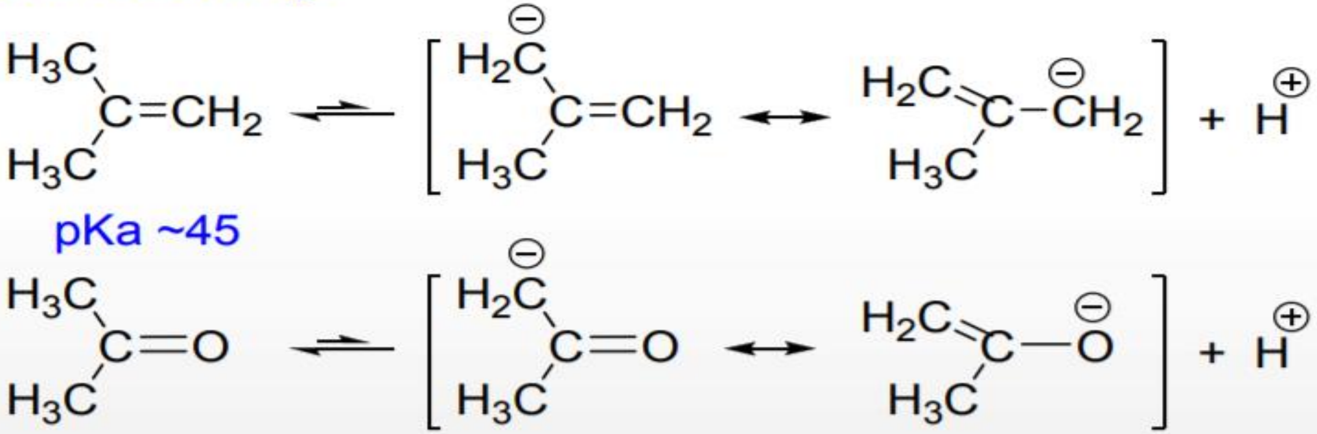


Resonance always results in a different distribution of electron density than would be the case if there were no resonance.

This decrease in electron density at one position (and corresponding increase elsewhere) is called the **resonance effect**.

A. Dipole moment

B. Acidity and basicity

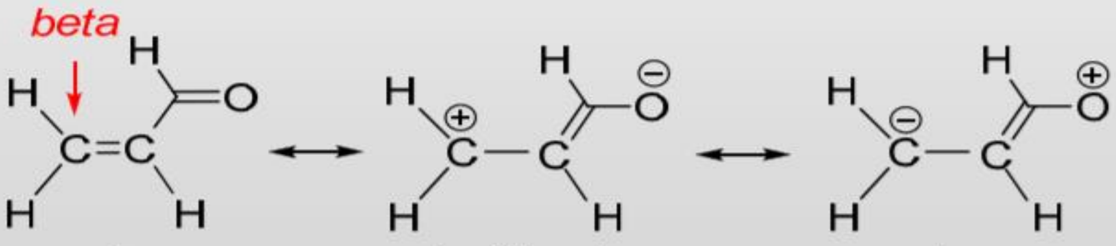


pKa ~45

pKa ~25

conjugated base

C. Spectrographic behavior and reactivity



major contributor

significant contributor

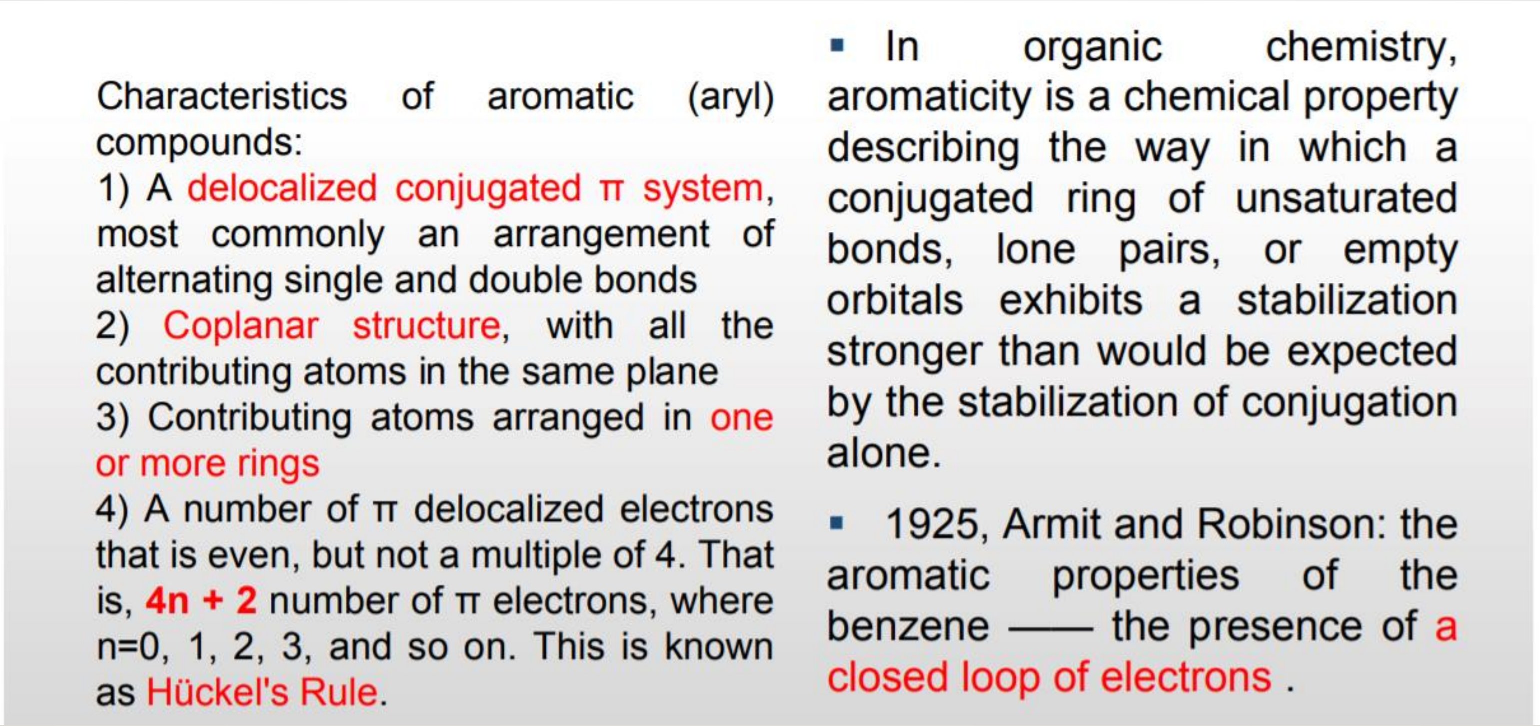
minor contributor

i) IR: C=O ~1690 cm^{-1} (1730 cm^{-1} for saturated compounds)

ii) ^{13}C NMR: β-C is less shielded, chemical shift (δ)↑

iii) nuclear attack at β-C

AROMATICITY



Characteristics of aromatic (aryl) compounds:

1) A delocalized conjugated π system, most commonly an arrangement of alternating single and double bonds

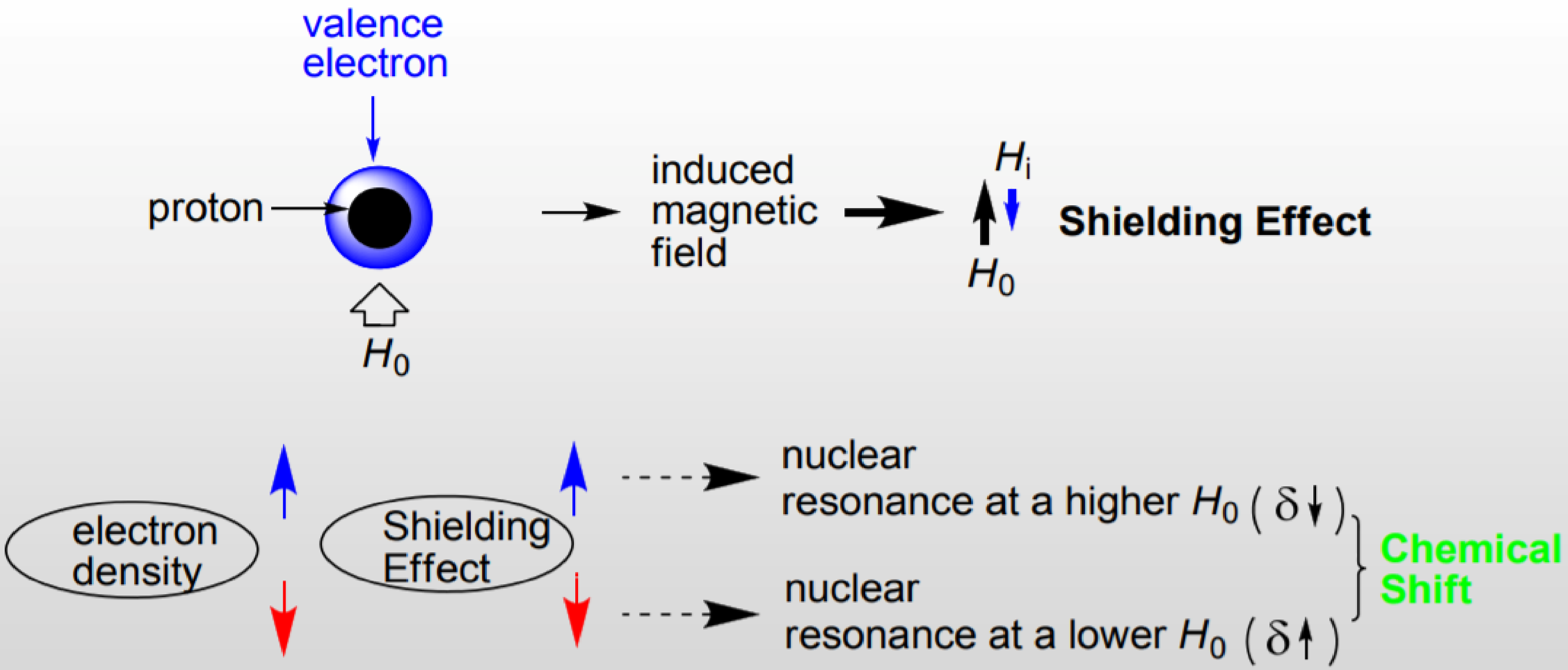
2) Coplanar structure, with all the contributing atoms in the same plane

3) Contributing atoms arranged in one or more rings

4) A number of π delocalized electrons that is even, but not a multiple of 4. That is, **4n + 2** number of π electrons, where n=0, 1, 2, 3, and so on. This is known as Hückel's Rule.

- In organic chemistry, aromaticity is a chemical property describing the way in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibits a stabilization stronger than would be expected by the stabilization of conjugation alone.
- 1925, Armit and Robinson: the aromatic properties of the benzene —— the presence of a closed loop of electrons .

NMR: determine experimentally whether or not a compound has a closed ring of electron.



valence electron

proton

H_0

induced magnetic field

H_i

H_0

Shielding Effect

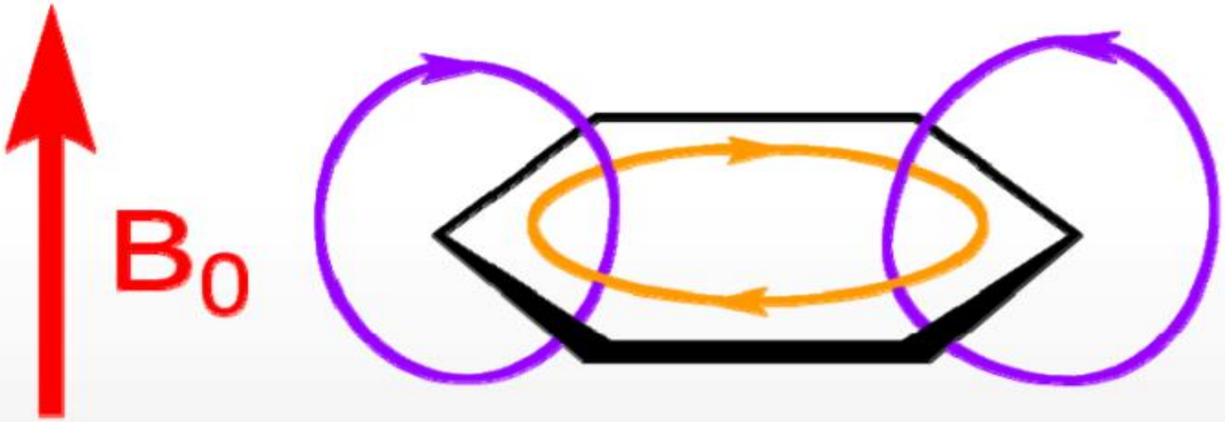
electron density

Shielding Effect

nuclear resonance at a higher H_0 ($\delta\downarrow$)

nuclear resonance at a lower H_0 ($\delta\uparrow$)

Chemical Shift



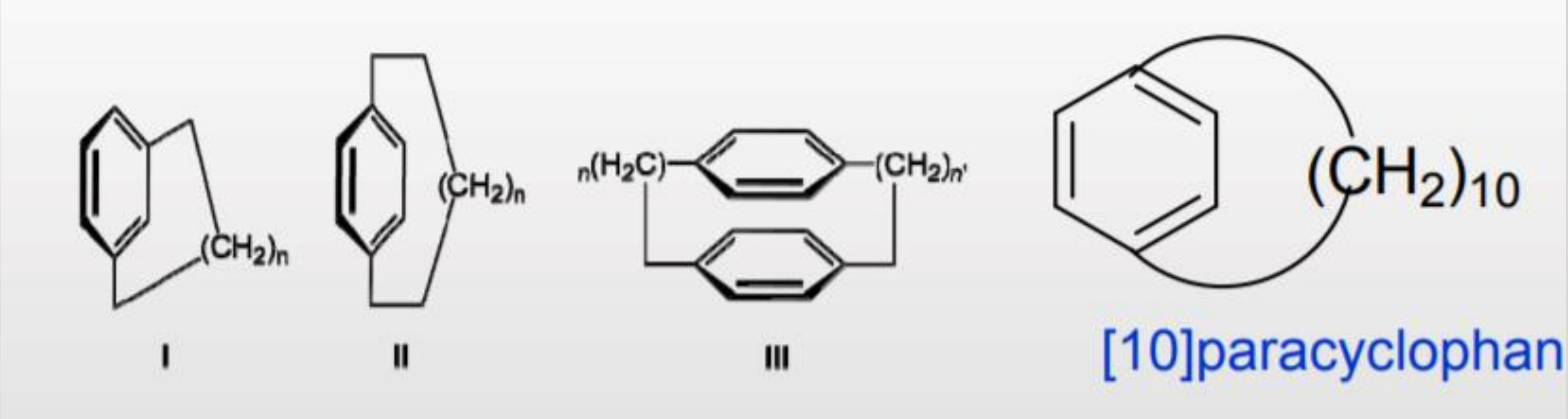
A diagram of an aromatic ring current. B_0 is the applied magnetic field, the red arrow indicating its direction. The orange ring shows the direction of the ring current, and the purple rings show the direction of the induced magnetic field.

i. ^{1}H NMR: the greater the density of the electron cloud surrounding a proton, the more upfield is its chemical shift (a lower δ value).

ii. The field "seen" by the aromatic protons is greater than it would have been in the absence of the diamagnetic ring current. The protons are moved downfield (to higher δ) compared to they would be if electron density were the only factor.

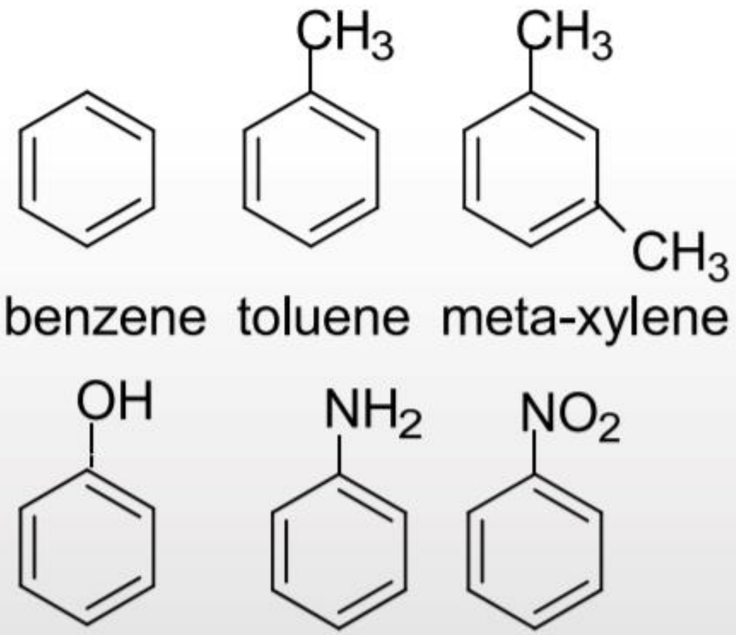
Aromaticity can be defined as the ability to sustain an induced ring current. A compound with this ability is called diatropic.

•Ordinary alkene hydrogens: ~ 5–6 ; cyclohexene 5.6 •The hydrogen atoms of benzene rings: ~ 7.3 •If there were protons above or within the ring, they would be subjected a decreased field and should appear at lower values than normal CH2 groups (normal for CH2 is ~1-2).



It follows that aromaticity can be determined from an nmr spectrum. If the protons attached to the ring are shifted downfield from the normal olefinic region, we can conclude that the molecule is diatropic and hence aromatic.

i. Six-member rings



benzene toluene meta-xylene

phenol aniline nitrobenzene

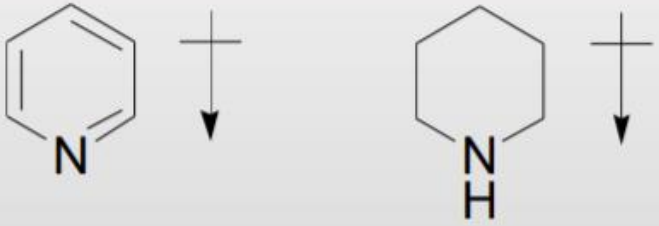
(Representative aromatic compounds)

NOTE

For nitrogen heterocyclics there are more significant canonical forms than for benzene.

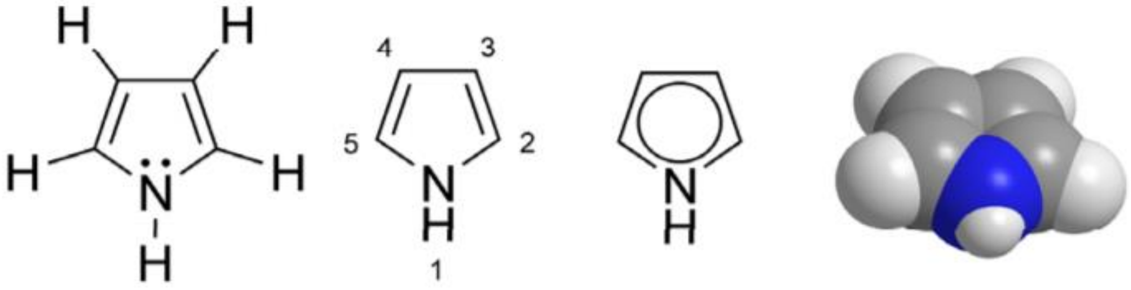
QUESTIONS

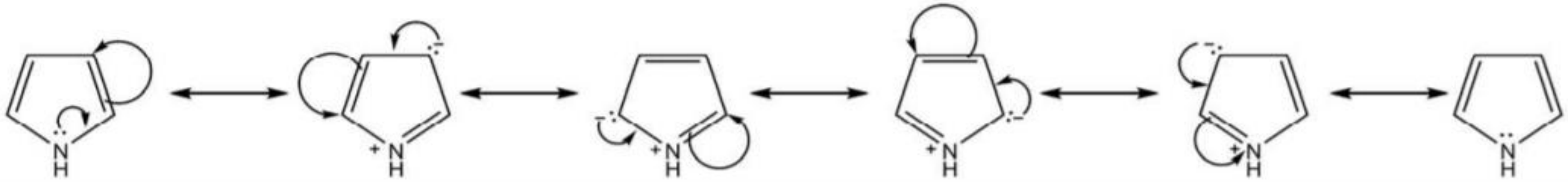
1) Dipole moment?



2.22D 1.17D

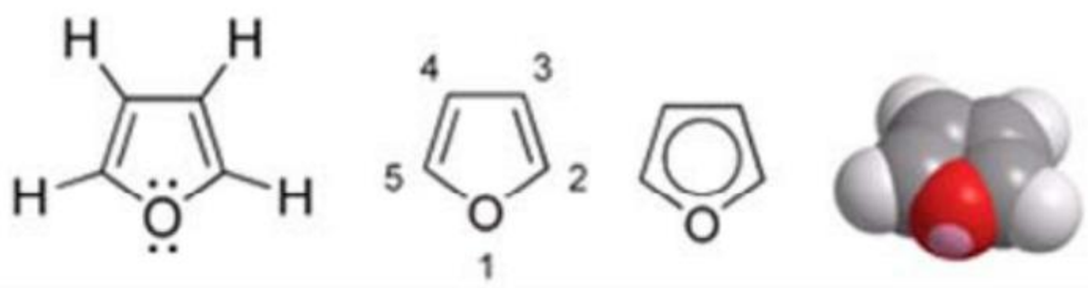
ii. Five-member rings

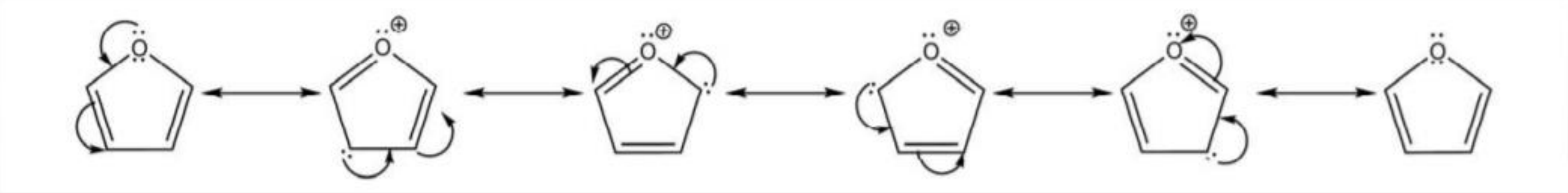


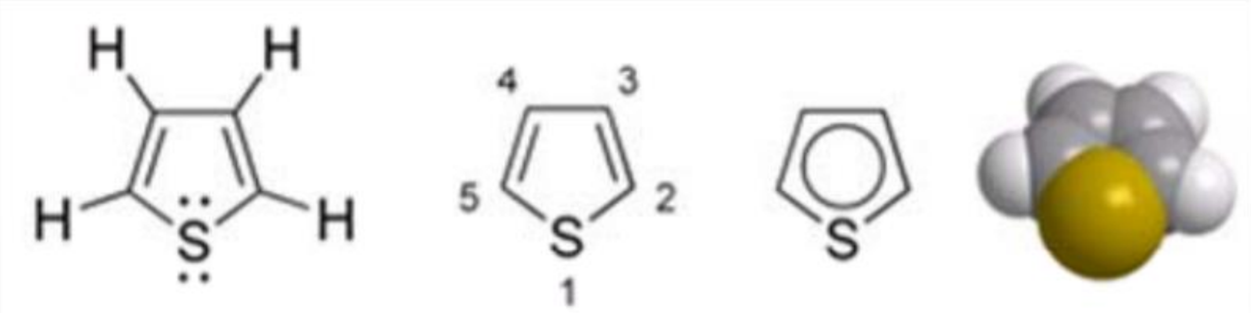


Resonance contributors of pyrrole

◆The N**H** proton in pyrroles is moderately acidic with a pK_a of 17.5.
◆Pyrrole undergoes electrophilic aromatic substitution predominantly at the 2 and 5 positions.

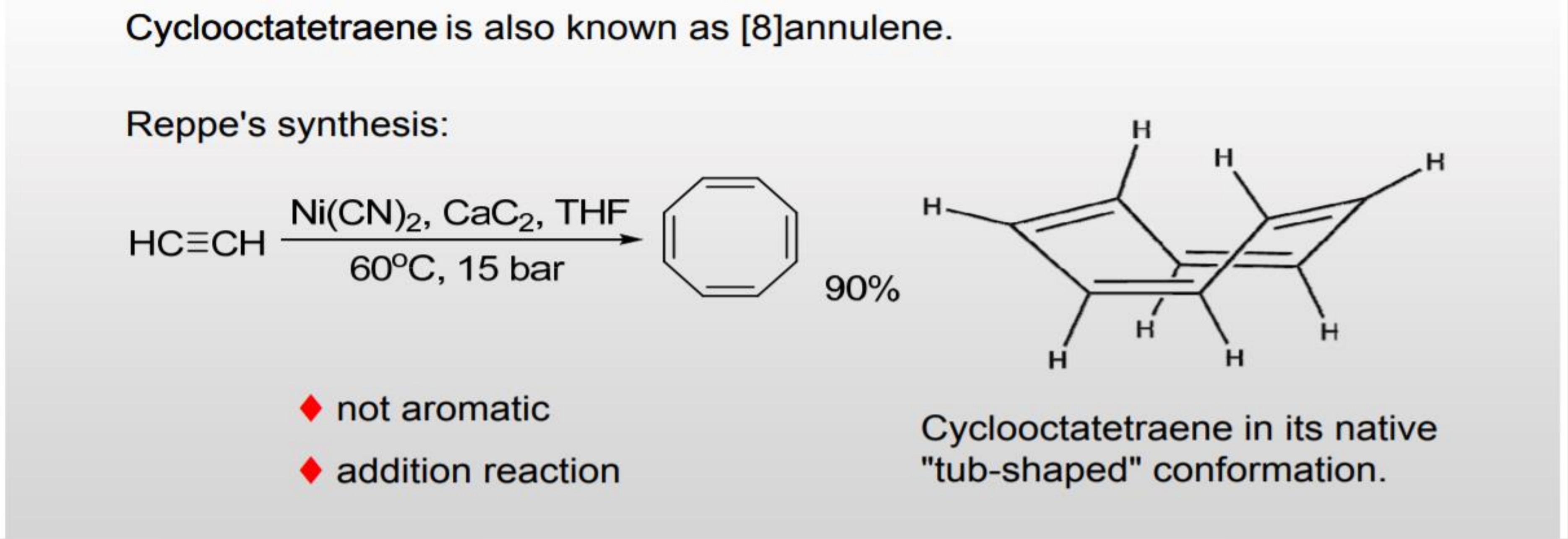

H
H
H
H
O
4
3
5
2
O
1
O


O
O
O
O
O
O


H
H
H
H
S
4
3
5
2
S
1
S

AROMATIC SYSTEMS WITH ELECTRON NUMBERS OTHER THAN 6

- Annulene are completely conjugated monocyclic hydrocarbons. They have the general formula CnHn (when n is an even number) or CnHn+1 (when n is an odd number).



Cyclooctatetraene is also known as [8]annulene.

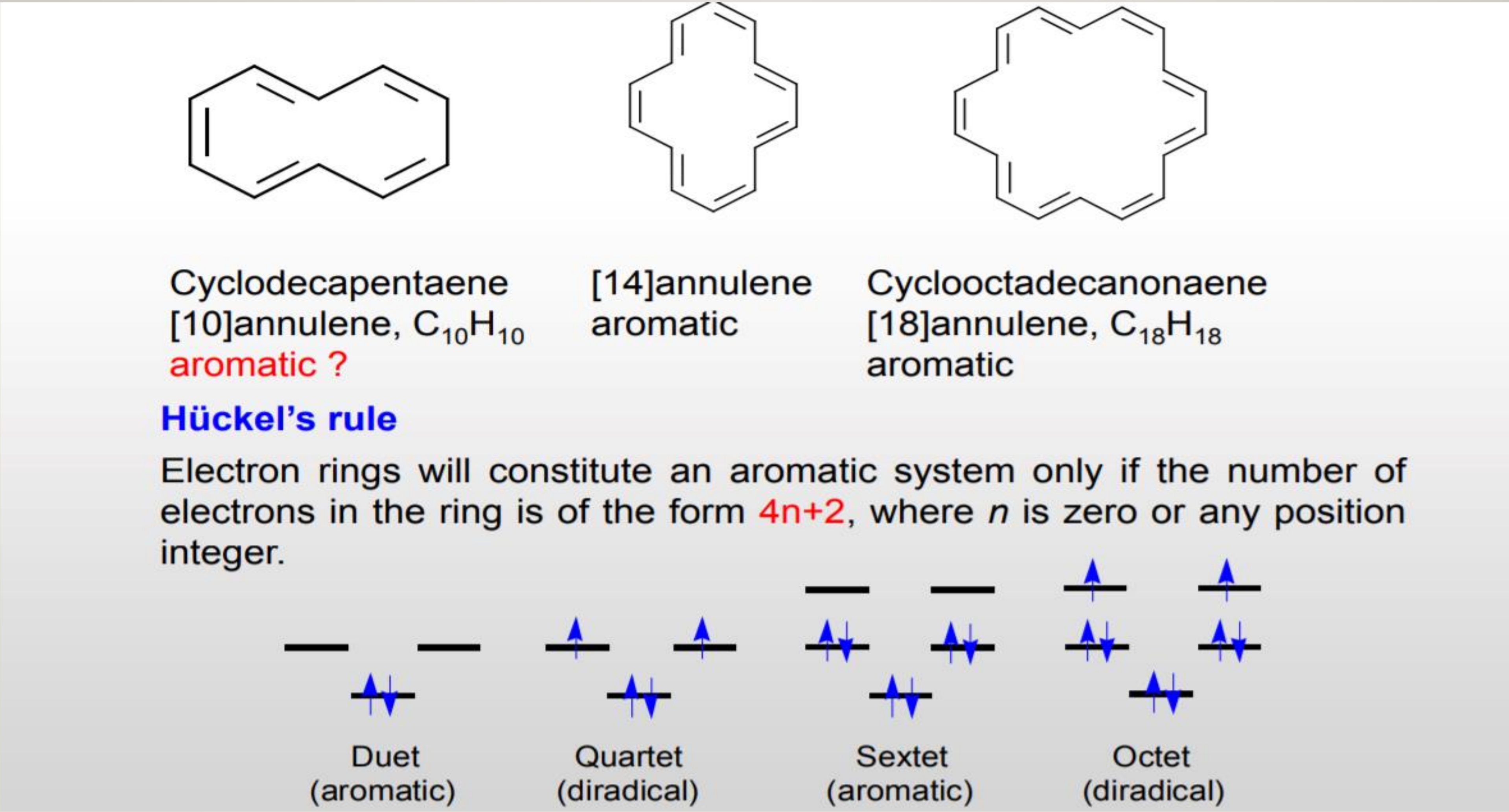
Reppe's synthesis:

$$HC\equiv CH \xrightarrow[60^{o}C,\ 15\ bar]{Ni(CN)_2,\ CaC_2,\ THF}$$ 90%

◆ not aromatic

◆ addition reaction

Cyclooctatetraene in its native "tub-shaped" conformation.



Cyclodecapentaene
[10]annulene, $C_{10}H_{10}$
aromatic ?

[14]annulene
aromatic

Cyclooctadecanonaene
[18]annulene, $C_{18}H_{18}$
aromatic

Hückel's rule

Electron rings will constitute an aromatic system only if the number of electrons in the ring is of the form 4n+2, where *n* is zero or any position integer.

Duet
(aromatic)

Quartet
(diradical)

Sextet
(aromatic)

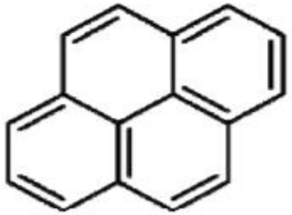
Octet
(diradical)

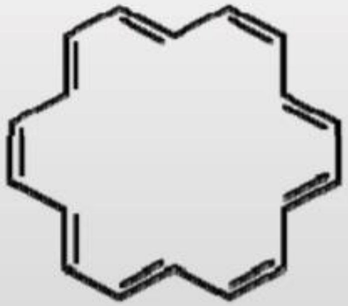
Hückel‘s rule is not valid for many compounds containing more than three fused aromatic nuclei in a cyclic fashion. For example, pyrene contains 16 conjugated electrons (8 bonds), and coronene contains 24 conjugated electrons (12 bonds). Both of these polycyclic molecules are aromatic even though they fail the $4n+2$ rule.

Look for aromaticity:

a) the presence of a diamagnetic ring current;
b) equal or approximately equal bond distances, except when the symmetry is disturbed by a hetero atom or other way;
c) planarity;
d) chemical stability;
e) the ability to undergo aromatic substitution.

Hückel’s rule can only be theoretically justified for monocyclic systems.

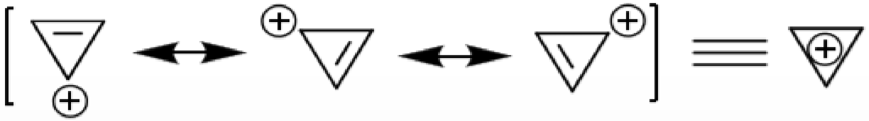


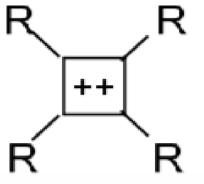


[18]annulene

Shiefing effect:
6 inner protons at −3 ppm

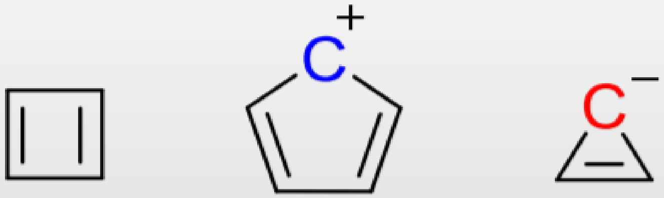
i. System of two electrons, 4*n*+2 (n =0)



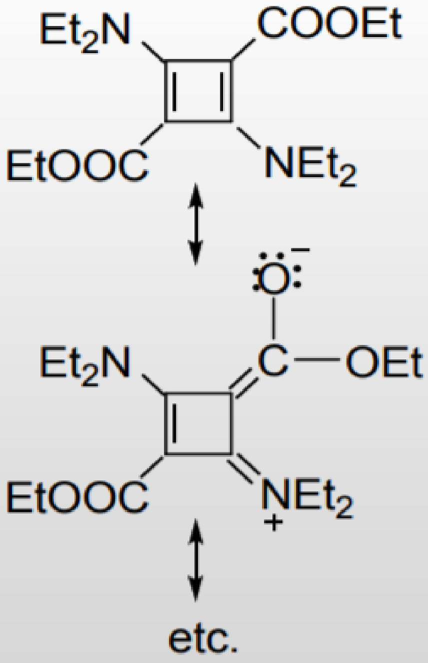


(R = Me, Ph)

ii. Systems of four electrons. Antiaromaticity



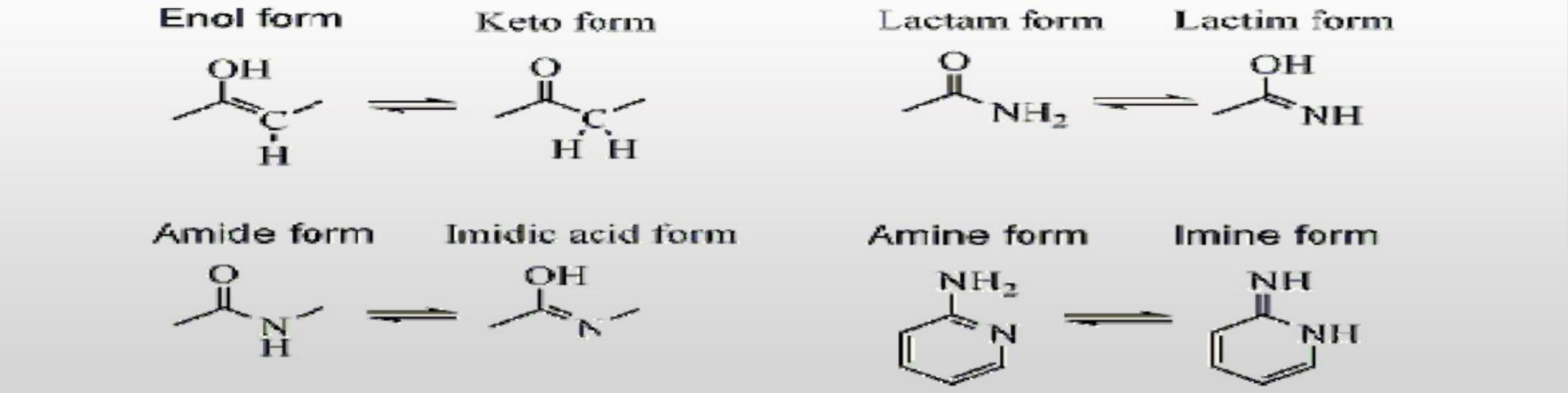
Antiaromatic molecules are cyclic systems containing alternating single and double bonds, where the pi electron energy of antiaromatic compounds is higher than that of its open-chain counterpart. IUPAC criteria: 4*n* π electrons, cyclic, planar, and a conjugated pi electron system.

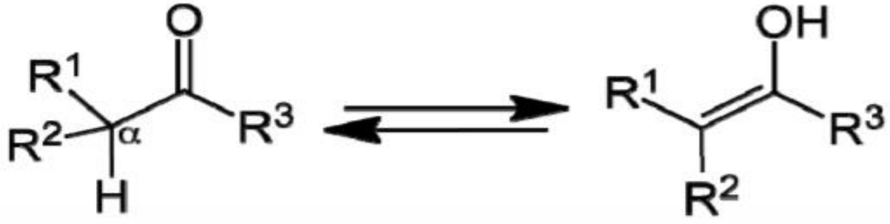


Push-pull effect

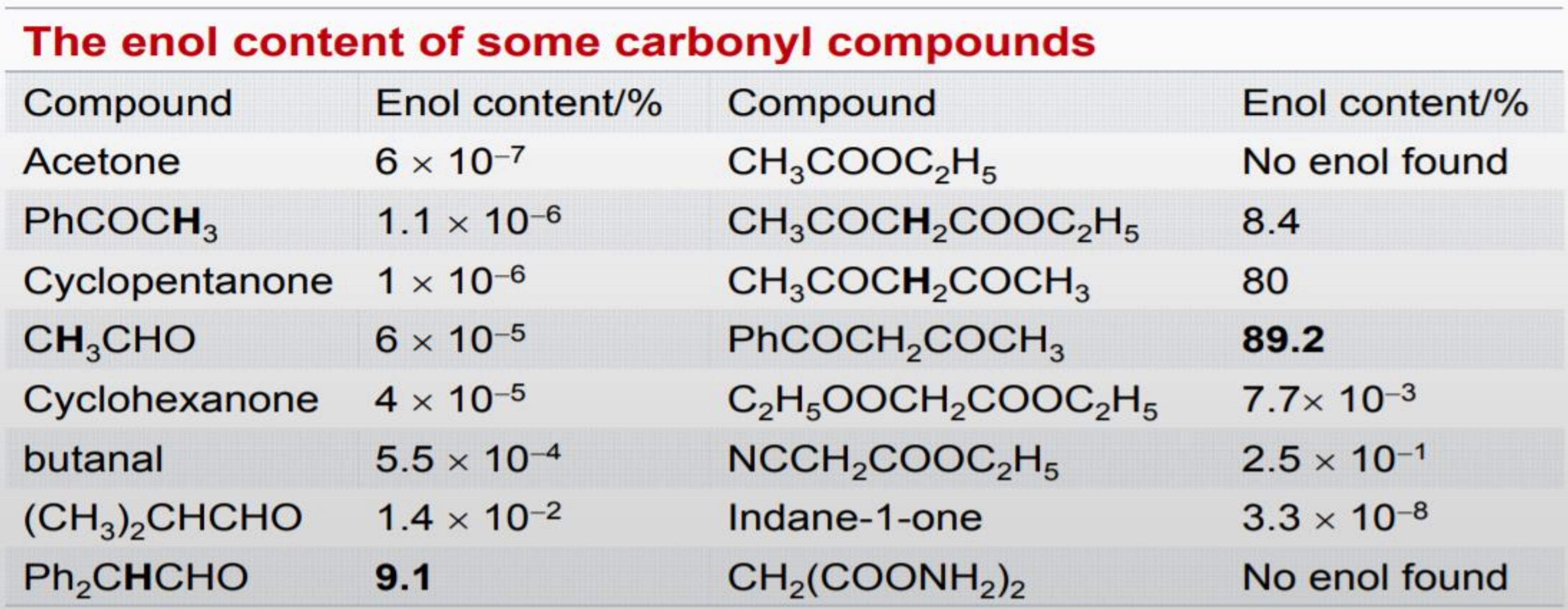
TAUTOMERISM

- Tautomers are isomers of organic compounds that readily interconvert by a chemical reaction called tautomerization. Commonly this reaction results in the formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond.



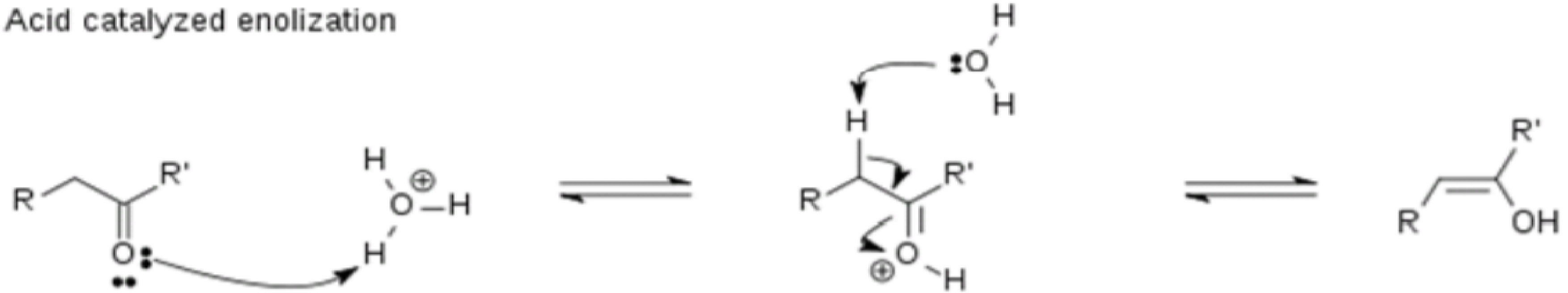


Keto-enol tautomerism.
keto form (left); enol
(right).

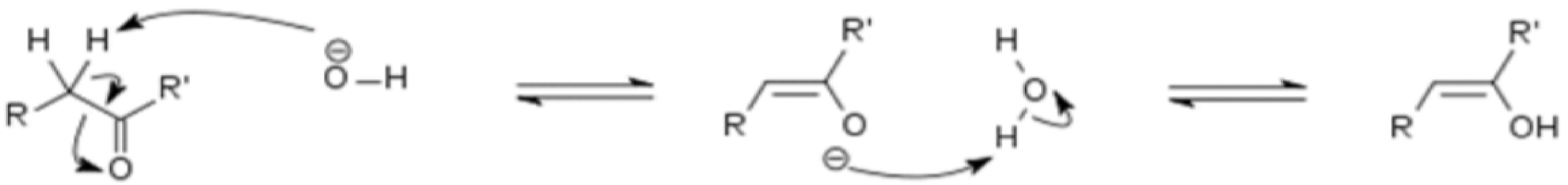


The enol content of some carbonyl compounds

Compound	Enol content/%	Compound	Enol content/%
Acetone	6×10^{-7}	$CH_3COOC_2H_5$	No enol found
$PhCOC\mathbf{H}_3$	1.1×10^{-6}	$CH_3COC\mathbf{H}_2COOC_2H_5$	8.4
Cyclopentanone	1×10^{-6}	$CH_3COC\mathbf{H}_2COCH_3$	80
$C\mathbf{H}_3CHO$	6×10^{-5}	$PhCOCH_2COCH_3$	**89.2**
Cyclohexanone	4×10^{-5}	$C_2H_5OOCH_2COOC_2H_5$	7.7×10^{-3}
butanal	5.5×10^{-4}	$NCCH_2COOC_2H_5$	2.5×10^{-1}
$(CH_3)_2CHCHO$	1.4×10^{-2}	Indane-1-one	3.3×10^{-8}
$Ph_2C\mathbf{H}CHO$	**9.1**	$CH_2(COONH_2)_2$	No enol found



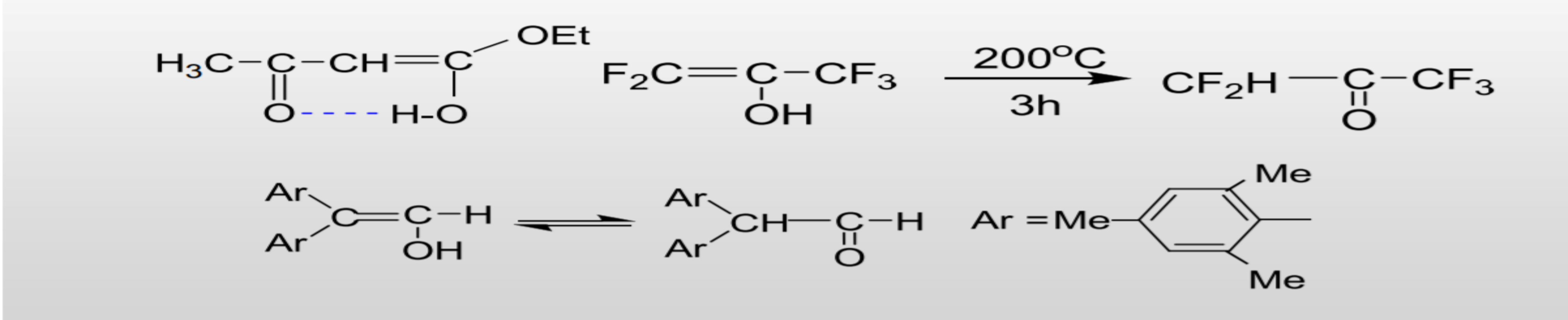
Acid catalyzed enolization



Base catalyzed enolization

THREE MAIN TYPES OF THE MORE STABLE ENOLS

- i. Molecules in which the enolic double bond is in conjugation with another double bond. The enol is also stabilized by internal hydro gen bonding.
- ii. Molecules that contain two or three bulky aryl groups.
- iii. Highly fluorinated enols



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