2.4
Electron Delocalization and Resonance Structures

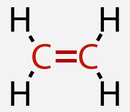
Reading Recommendations

- Clayden, Greeves, Warren, *Organic Chemistry*, Oxford University Press, 2nd ed., **2012**, *pp* 141–162.
- Jamart, Bodiguel, Brosse, *Les cours de Paul Arnaud - Cours de chimie organique*, Dunod, 19th ed., **2015**, *pp* 87–97.

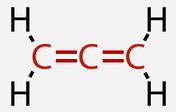
Molecules with Several Multiple Bonds

- bond lengths for single and double bonds, energy barriers for rotation for single bonds

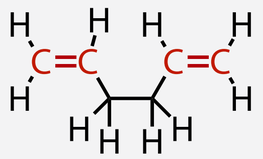
1.33 Å



1.33 Å 1.33 Å

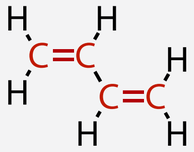


1.33 Å 1.33 Å



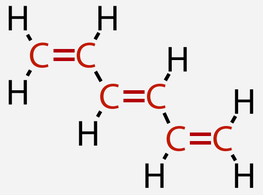
1.54 Å ⟳ 3 kJ/mol

1.34 Å 1.34 Å



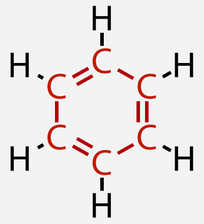
1.47 Å ⟳ 30 kJ/mol

1.34 Å 1.37 Å 1.34 Å



1.46 Å 1.46 Å ⟳ 30 kJ/mol

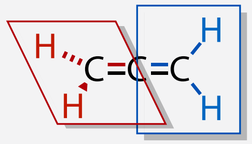
1.45 Å (all bonds)



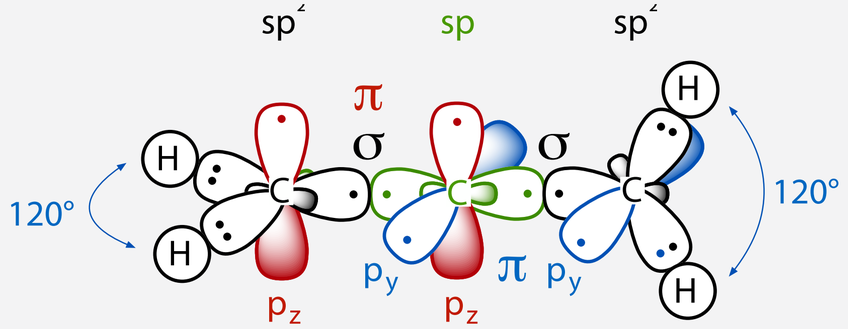
- **alternating double and single bonds are called conjugated double bonds**
- **conjugated double bonds are longer than normal**
- **single bonds between conjugated double bonds are shorter and have a high rotation barrier**

Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

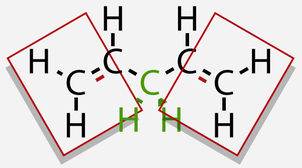
- “cumulated double bonds” are in orthogonal planes, do not interact electronically



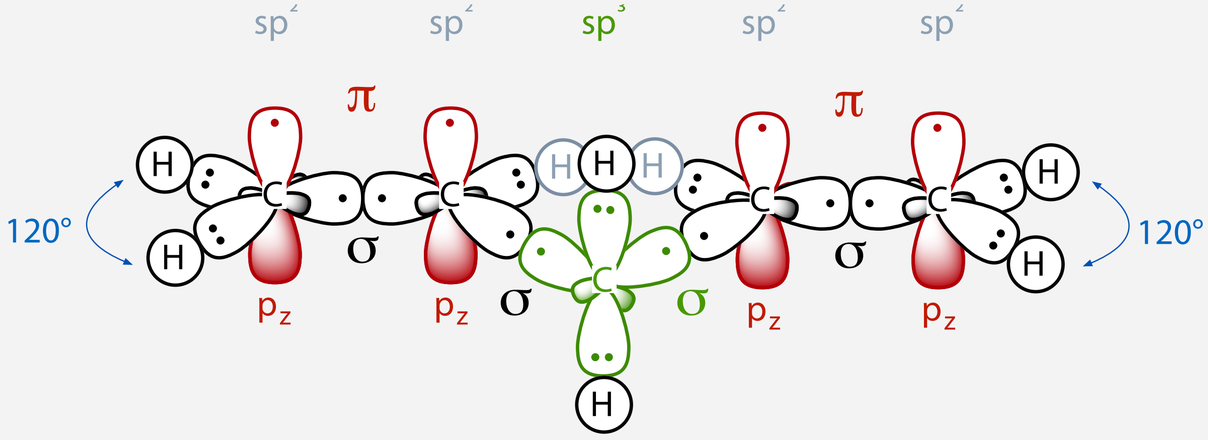
1,2-propadiene



- “isolated double bonds” separated by sp^3 carbons are in arbitrary planes, do not interact



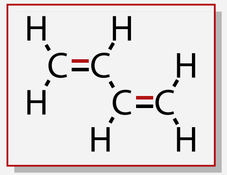
1,5-pentadiene



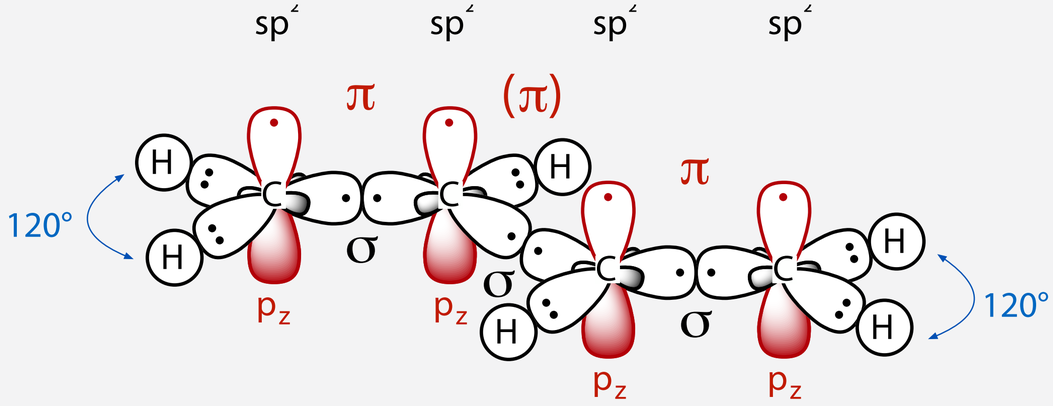
- **neither cumulated nor isolated multiple bonds “communicate”, i.e., interact electronically**

Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

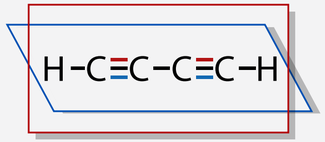
- “conjugated double bonds” are in the same plane and p_z orbitals are in direct contact



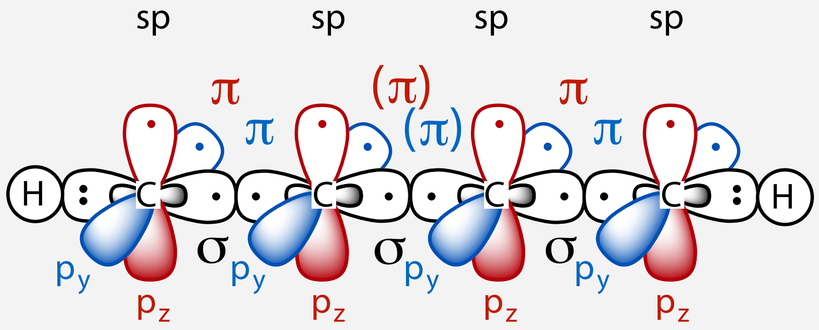
1,3-butadiene



- “conjugated triple bonds” are in the same planes, pz and py orbitals are in direct contact



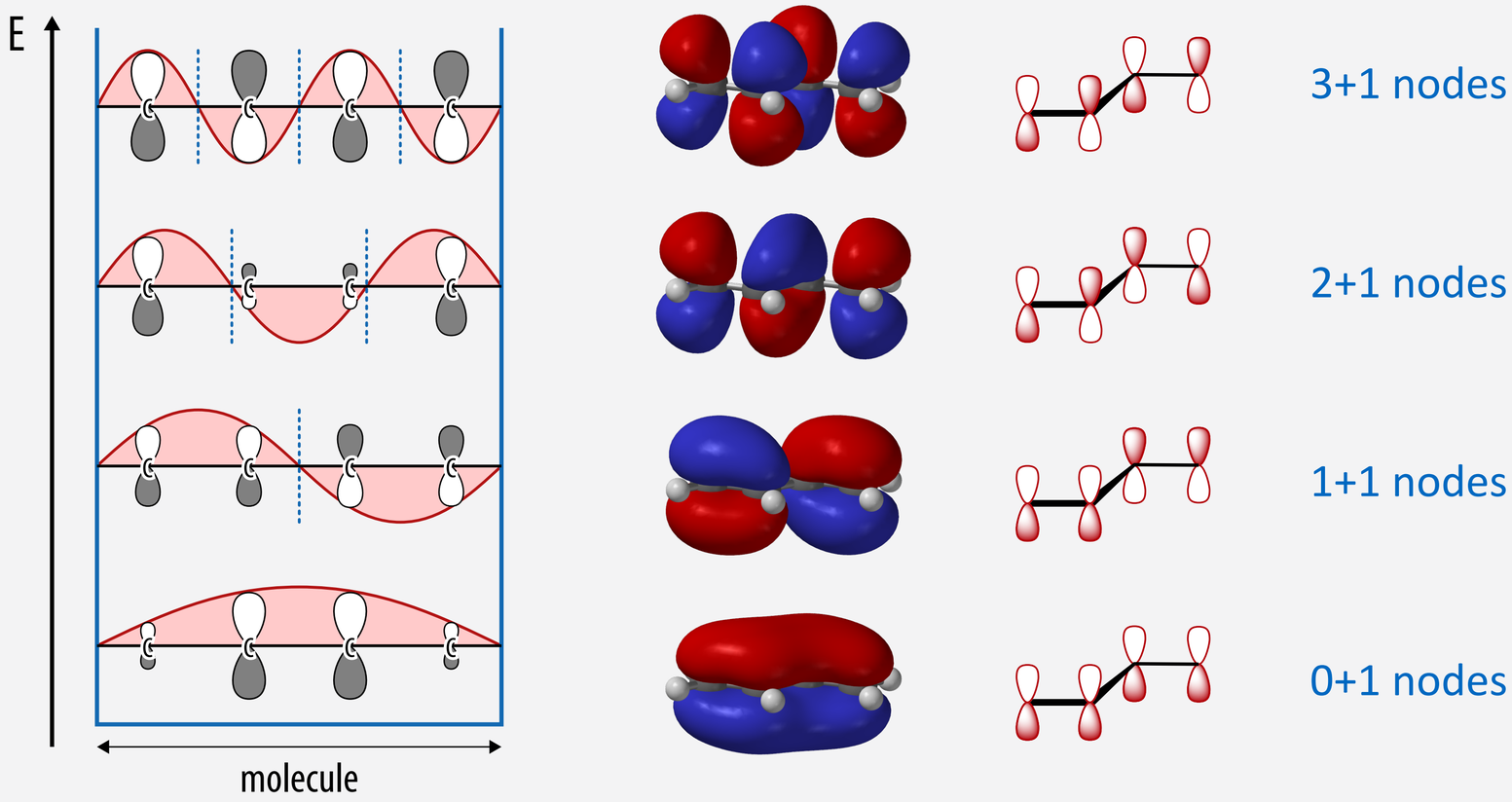
1,3-butadiyne



- **alternating double / triple and single bonds are called “conjugated multiple bonds”**
- **conjugated multiple bonds interact with each other electronically, electrons are delocalized**

“Electron in a 1D Box” Model for a Linear π-Conjugated Systems

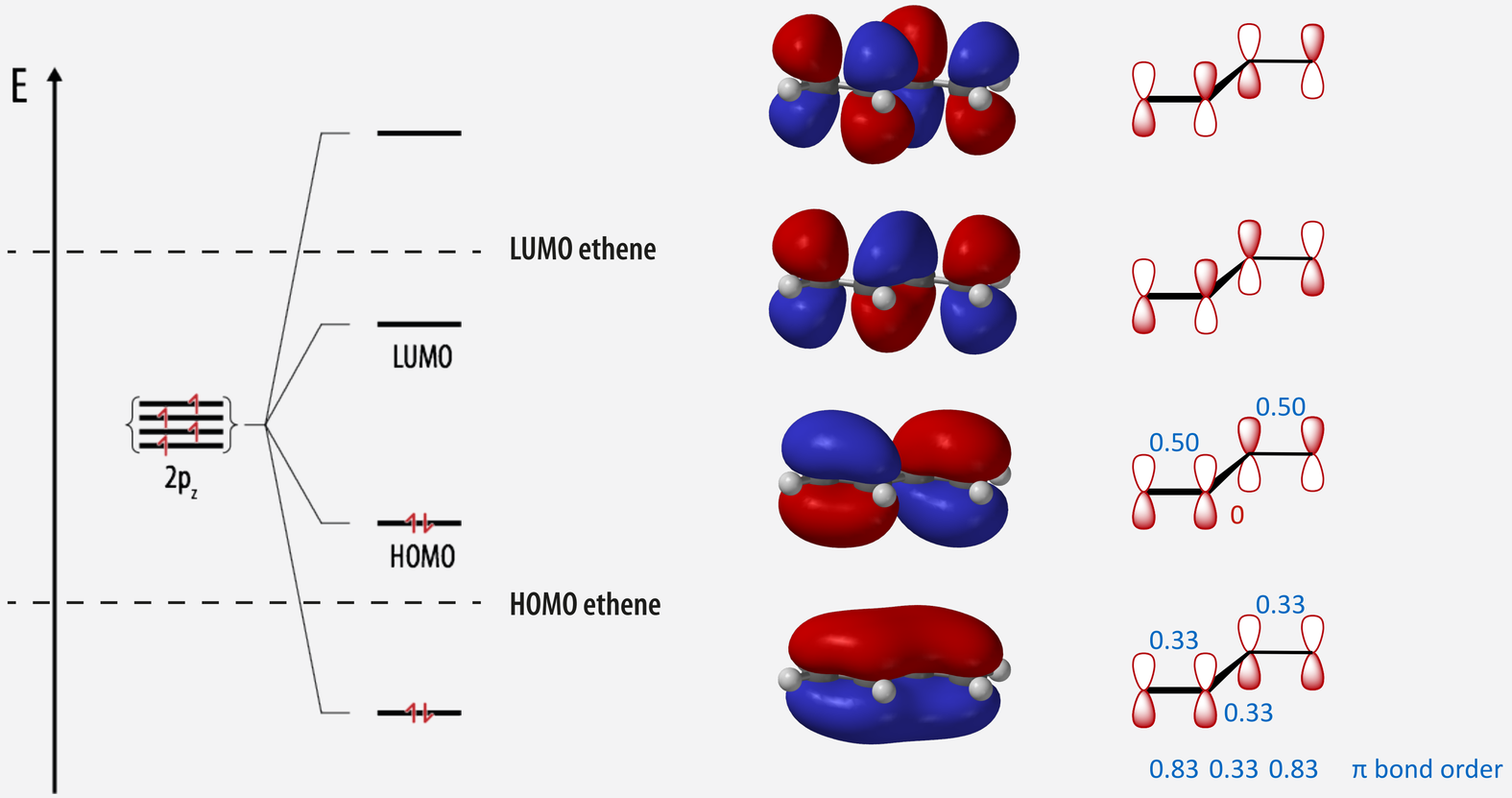
- “electron in 1D Box with infinite potential well” is a model for linear π-conjugated systems



- **linear combination of four $2p_z$ orbitals results in a set of four molecular orbitals**
- **resulting molecular π-orbitals are delocalized over all four carbon atoms**
- **energy successively increases with number of node planes in the π-system**

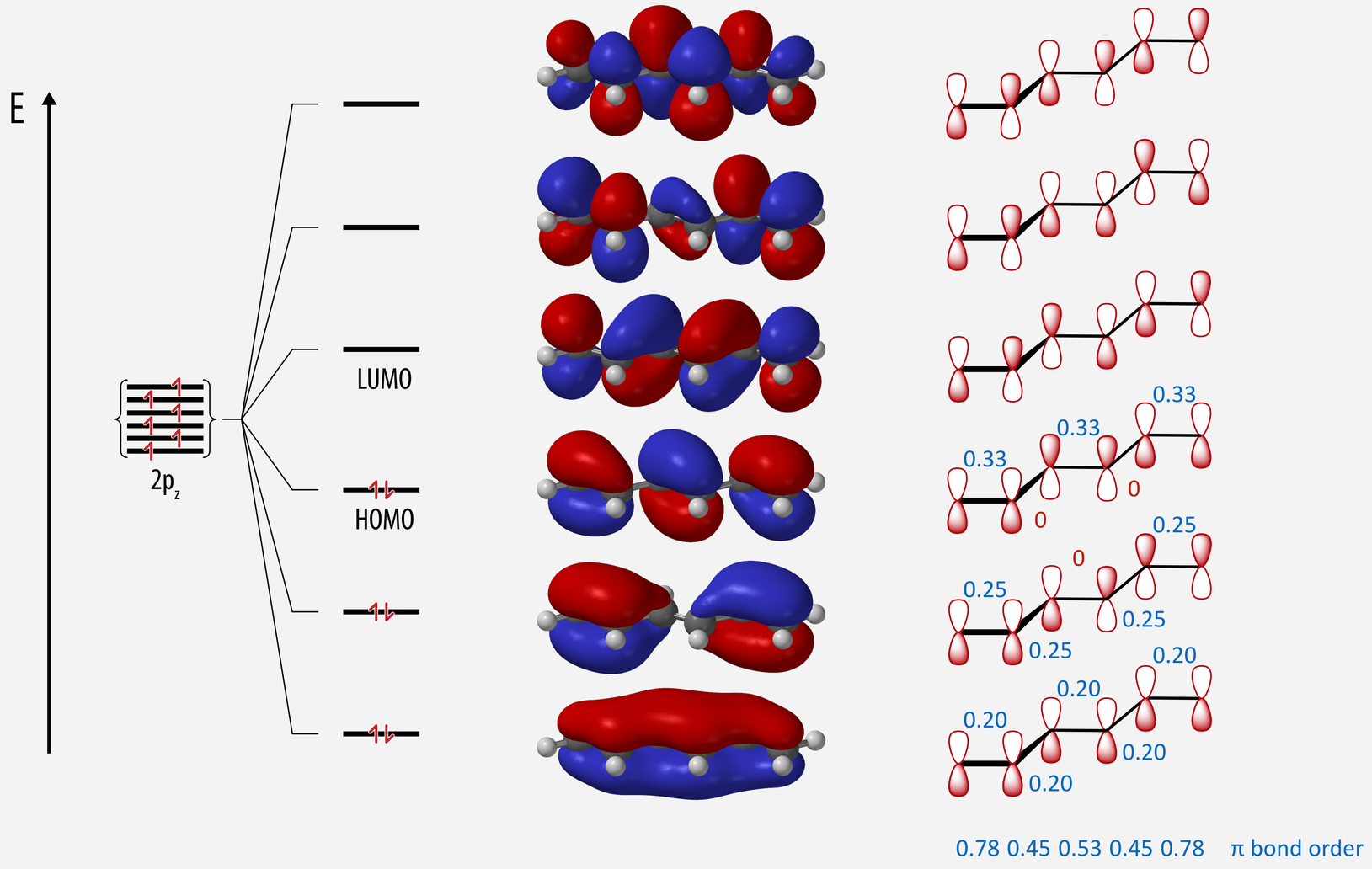
Frontier Orbitals and Bond Orders in 1,3-Butadiene

- simplified and schematic MO energy diagram of the frontier orbitals of 1,3-butadiene



- **double bonds have bond order <2, central single bond >1, restricted rotation (30 kJ/mol)**
- **sum of all π MO lower in energy than in ethene, butadiene "more stable"**
- **HOMO less stabilized, HOMO-LUMO gap smaller than in ethene, butadiene "more reactive"**

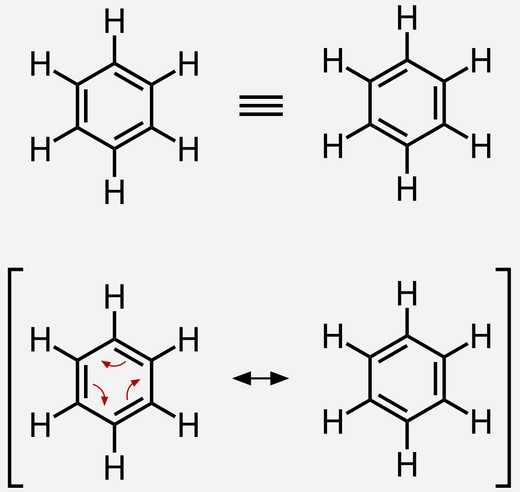
Frontier Orbitals and Bond Orders in 1,3,5-Hexatriene

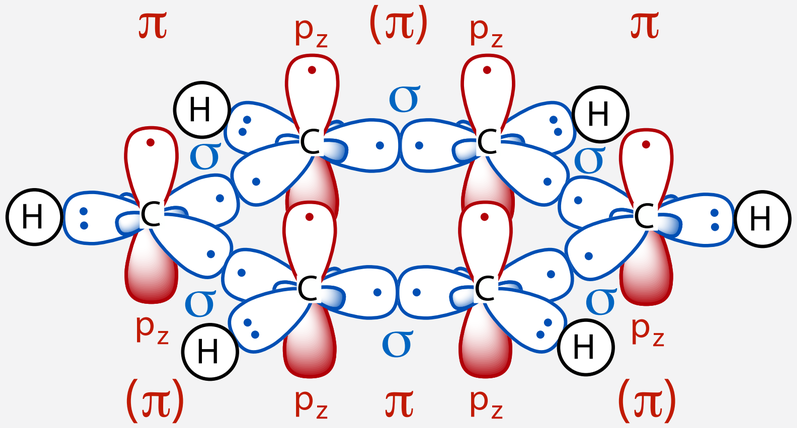


- **all π-electrons delocalized over entire molecule**
- **HOMO/LUMO gap decreases, bond order of bonds converges to 1.5**

Electron Delocalization in Cyclic π-Conjugated Multiple Bonds

- electron delocalization particularly pronounced for “cyclic conjugated double bonds”

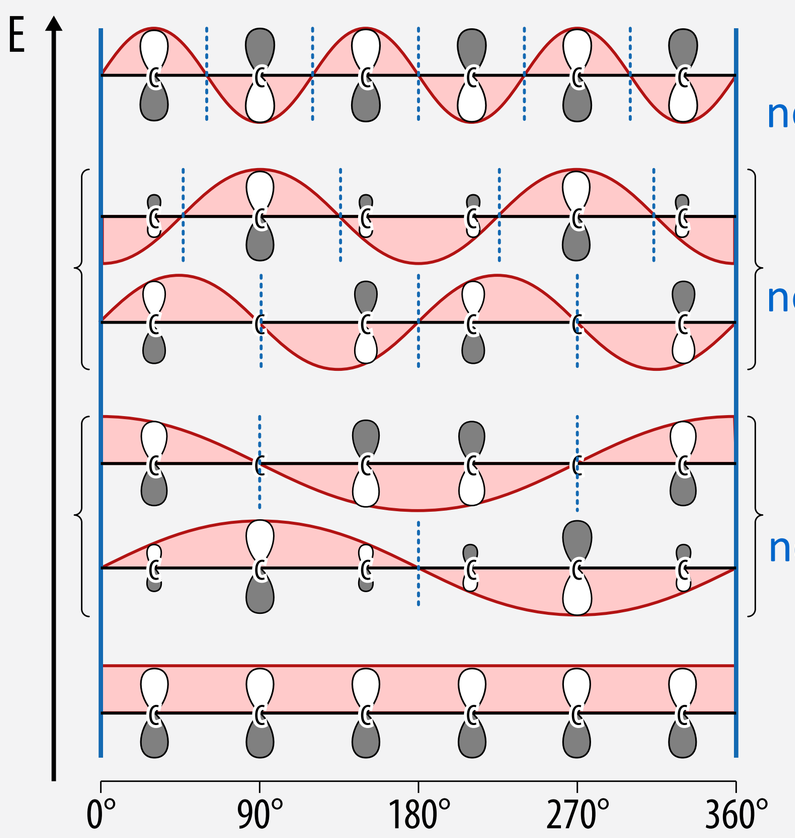


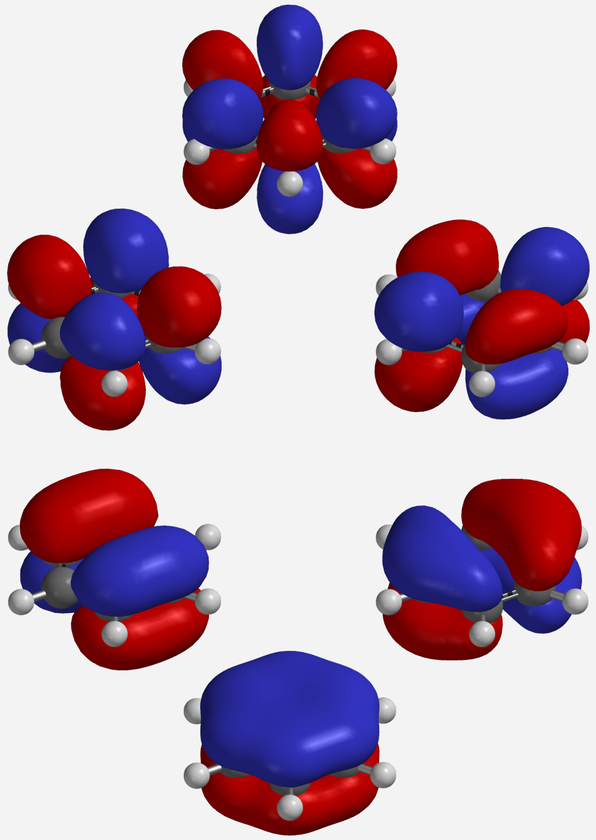


- **cyclic conjugated double bonds can be represented by (neutral) resonance structures**
- **all bonds are symmetrically equivalent, equal bond length 1.45 Å, bond order 1.5**
- **“aromatic” compounds with 2n+1 cyclic conjugated double bonds are particularly stable**

“Electron in a 1D Box” Model for Cyclic π-Conjugated Systems

- “electron in a box with steady boundary condition” is a model for cyclic π-conjugated systems

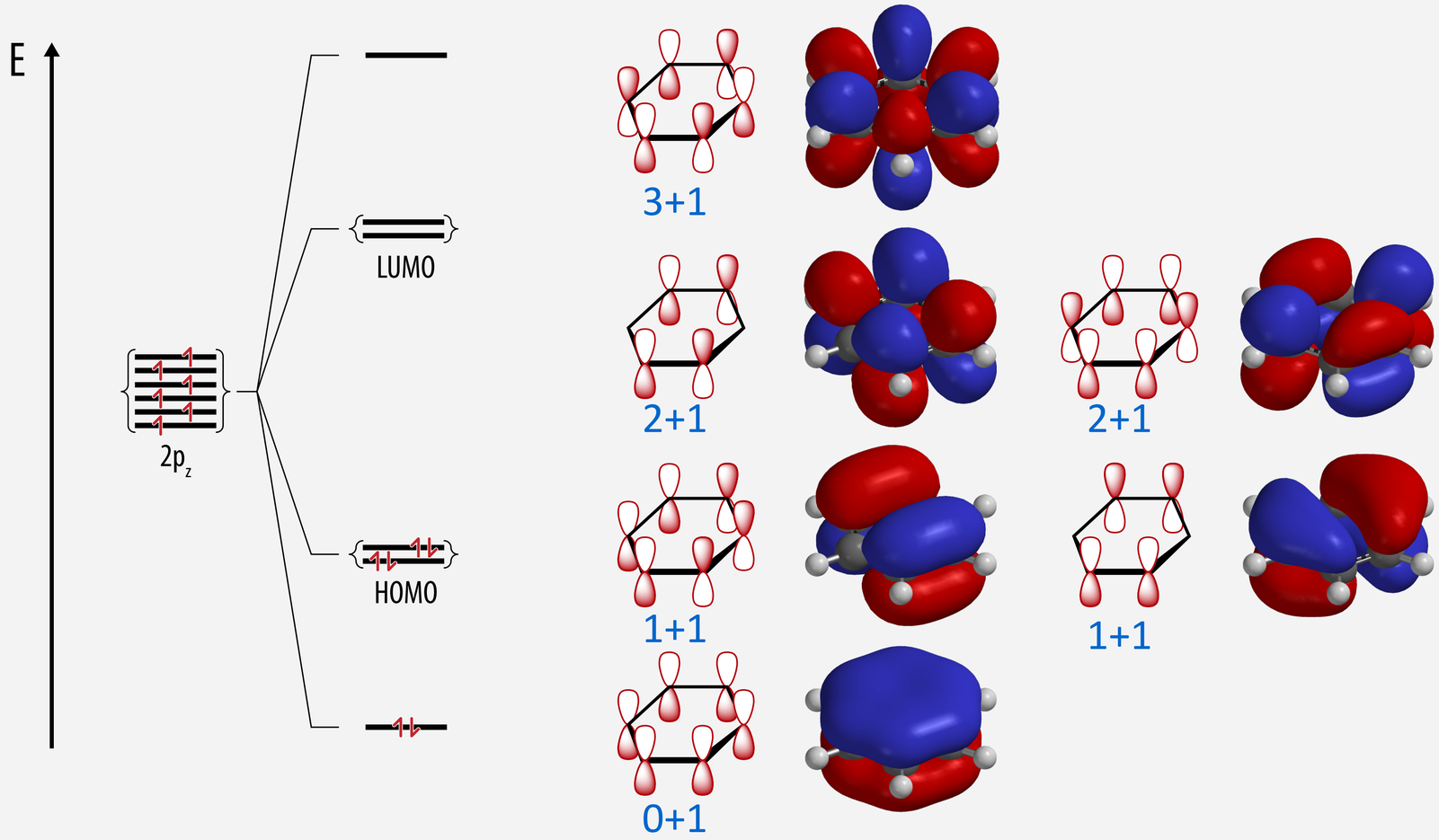




- **all π-orbitals extend over all six carbons, “do not look like” double bond MO at all**
- **two degenerate (identical in energy and symmetry) HOMOs better stabilized than in ethene**
- **aromatic π-systems are particularly stable, molecules are less reactive**

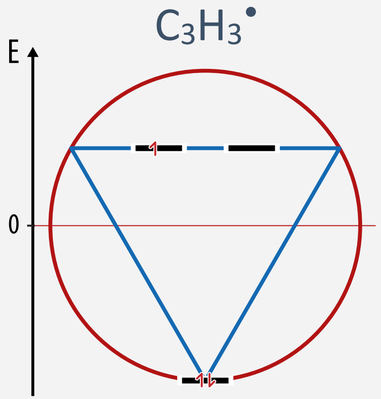
“Electron in a 1D Box” Model for Cyclic π-Conjugated Systems

- “electron in a box with steady boundary condition” is a model for cyclic π-conjugated systems

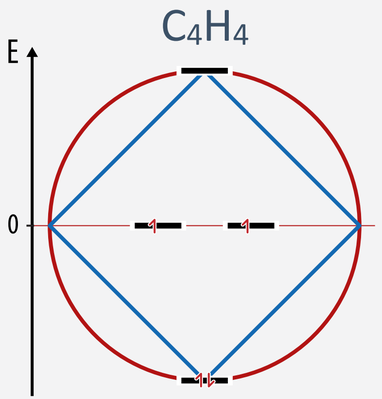


- **benzene shows no bond length alternation, there are no double bonds**
- **all six carbon bonds are equal, bond order 1.5**

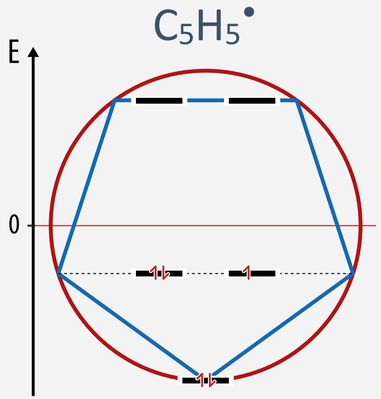
Approximation for the MO Energy Diagrams of Cyclic π-Conjugated Systems



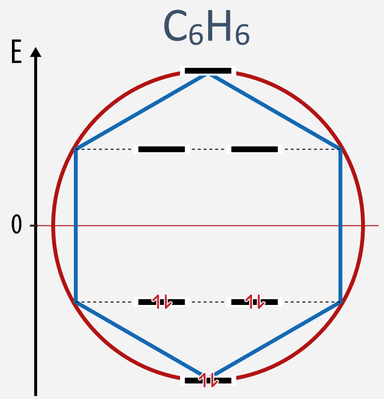
very unstable
open shell, destabilized



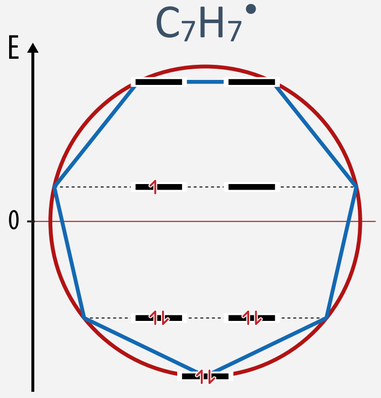
very unstable
open shell, destabilized



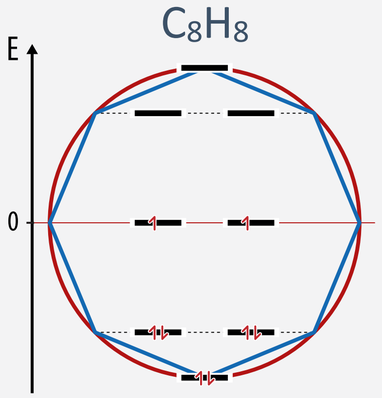
unstable
open shell, stabilized



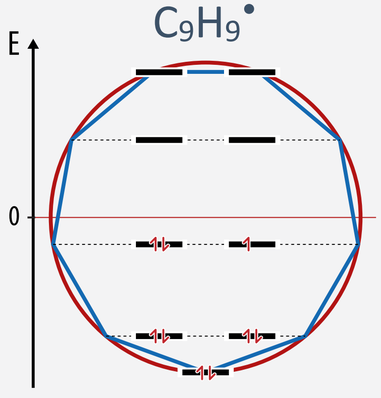
very stable
closed shell, stabilized



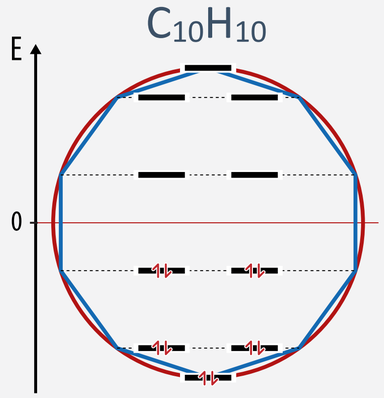
very unstable
open shell, destabilized



very unstable
open shell, destabilized



unstable
open shell, stabilized



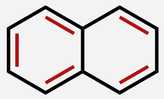
very stable
closed shell, stabilized

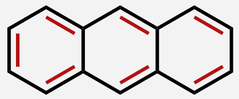
- **Hückel rule for "aromaticity": monocyclic conjugated systems with $4n+2$ electrons**

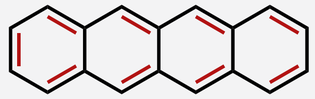
Examples of Aromaticity and Aromatic Compounds

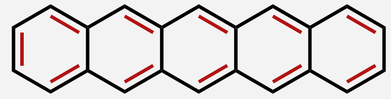
- "aromaticity" is a historically derived concept to describe "unusual" chemical stability

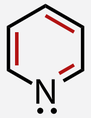
benzene  6π

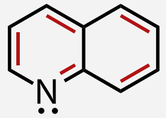
naphthalene  10π

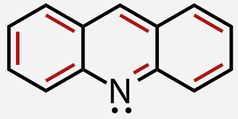
anthracene  14π

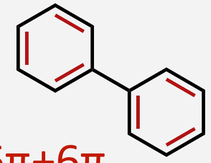
tetracene  18π

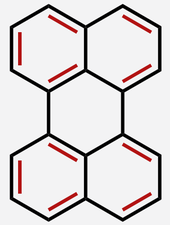
pentacene  22π

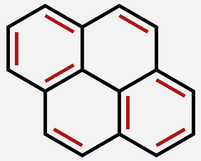
pyridine  6π

quinoline  10π

acridine  14π

biphenyl  6π+6π

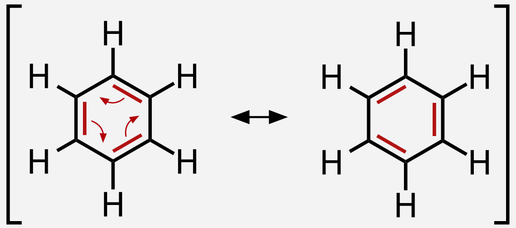
perylene  10π+10π

pyrene  16π

- **only benzene strictly fulfills Hückel definition of aromaticity (monocyclic, 4n+2 π electrons)**
- **in a broader sense, all compounds with cyclic conjugated π-systems are called "aromatic"**
- **including compounds with heteroatoms, or systems with 4n π electrons (less stable)**

Representing Delocalization with Resonance Structures

- **delocalization of cyclic π-systems can be represented by neutral resonance structures**



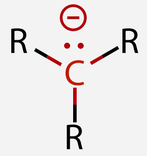
- **drawing the neutral resonance structures of cyclic π-conjugated systems:**
  - draw σ bond framework of sp^2-hybridized carbons/heteroatoms (and attached atoms)
  - draw the π electron pairs of the double bonds (ideally in another color)
  - indicate with arrows how to flip π electron pair to adjacent single bond
  - only π electron pairs can be moved; never change σ bond framework
  - respect the valency rules; carbon atoms must never become pentavalent
  - enclose resonance structures in square brackets and link with double arrows

- **resonance structures are just representations of delocalization**

- **π electrons do not really move/resonate**

Representing Delocalization with Resonance Structures

- zwitterionic resonance structures comprise positive/negative formal charges

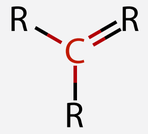


carbanion

trivalent

5 electrons
negative formal charge

3 bonds, 1 electron pair
octet rule fulfilled

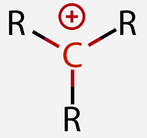


double-bonded carbon

tetravalent

4 electrons
neutral

4 bonds
octet rule fulfilled



carbocation

trivalent

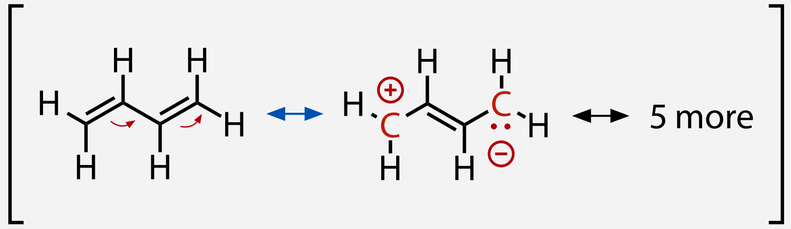
3 electrons
positive formal charge

3 bonds
electron sextet (deficient)

- **formal charges are determined by homolytic bond cleavage and counting electrons**
- **valency determined by counting electron pairs involved in covalent bonds to other atoms**
- **octet rule always respected: stable carbon always tetravalent, never pentavalent**
- **reactive states/intermediates can be trivalent; sextet possible but electron deficient**

Representing Delocalization with Resonance Structures

- **representing delocalization in linear systems requires zwitterionic resonance structures**

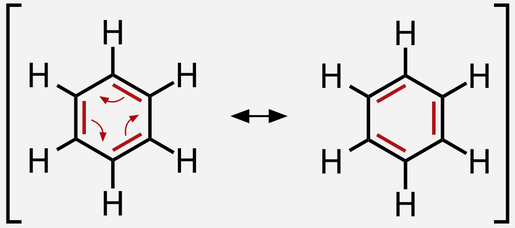


- **drawing the zwitterionic resonance structures of linear π-conjugated systems:**
  - draw σ bond framework of sp^2-hybridized carbons/heteroatoms (and attached atoms)
  - draw the π electron pairs of the double bonds (ideally in another color)
  - indicate with arrows how to flip π electron pair to adjacent single bond
  - alternatively, move π electron pair to become free electron pair on adjacent carbon atom
  - only move π electron pairs; never change σ bond framework
  - respect the valency rules; add formal charges to indicate missing/excess electrons
  - enclose resonance structures in square brackets and link with double arrows
- **resonance structures are representations of delocalization**
- **π electrons do not really move/resonate**

Using Resonance Structures to Compare Delocalization

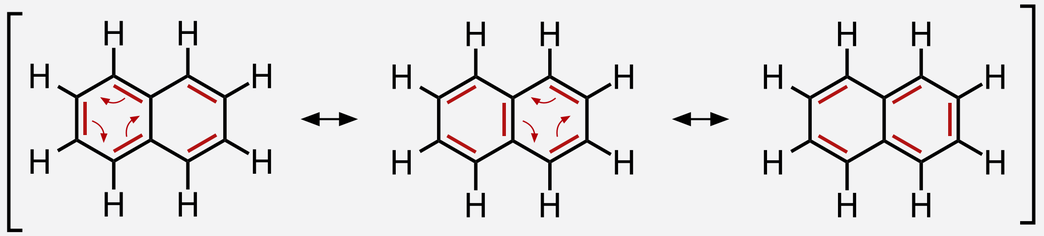
- **degree of delocalization can be estimated from total number of resonance structures**

benzene



two neutral resonance structures

naphthalene



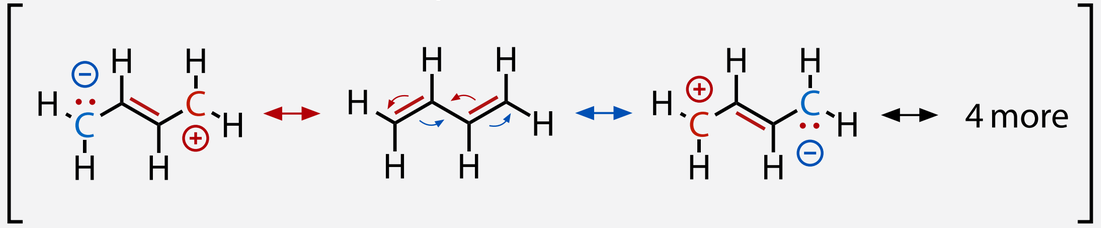
three neutral resonance structures

- **degree of delocalization increases with number of neutral resonance structures**

Using Resonance Structures to Compare Delocalization

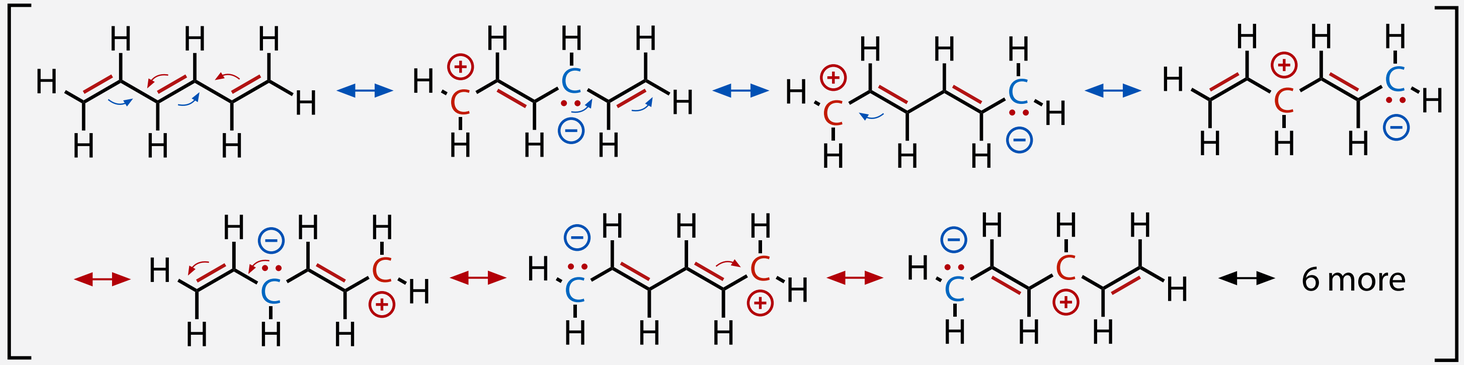
- **degree of delocalization can be estimated from total number of resonance structures**

1,3-butadiene



one neutral (major), six zwitterionic (minor) resonance structures

1,3,5-hexatriene



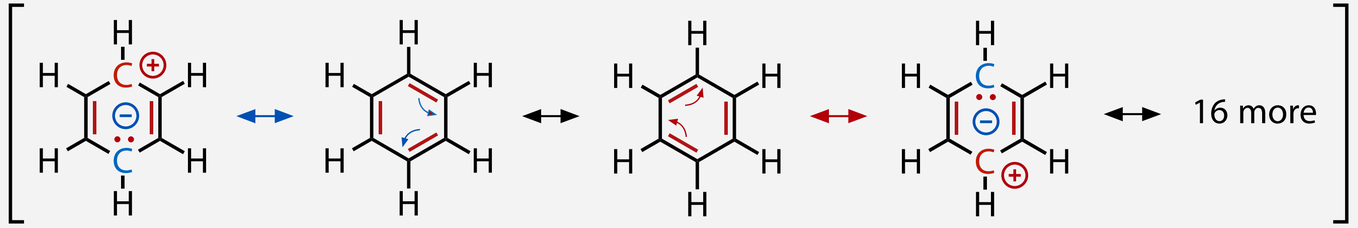
one neutral (major), twelve zwitterionic (minor) resonance structures

- **degree of delocalization increases with number of zwitterionic resonance structures**

Using Resonance Structures to Compare Delocalization

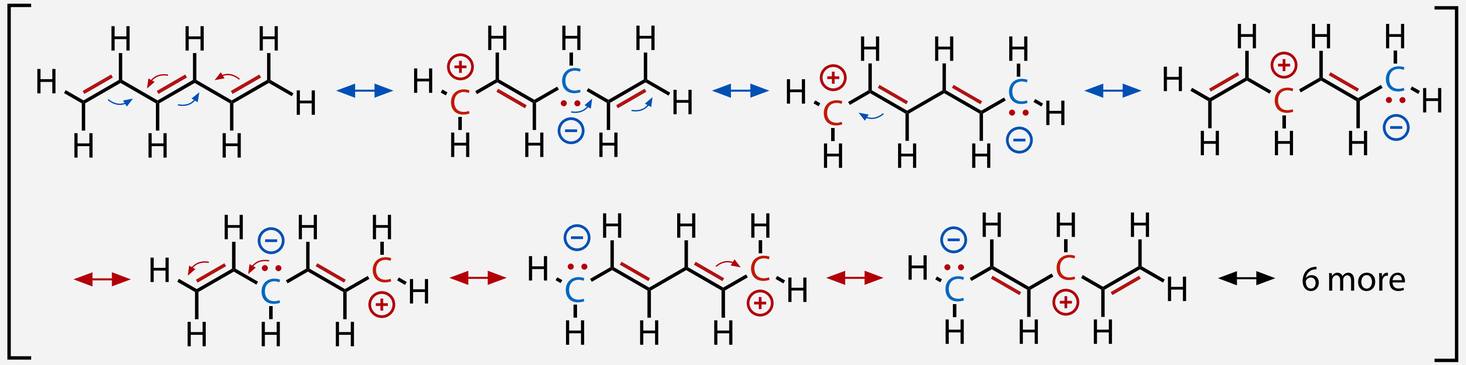
- **degree of delocalization can be estimated from total number of resonance structures**

benzene



two neutral (major), eighteen zwitterionic (minor) resonance structures

1,3,5-hexatriene



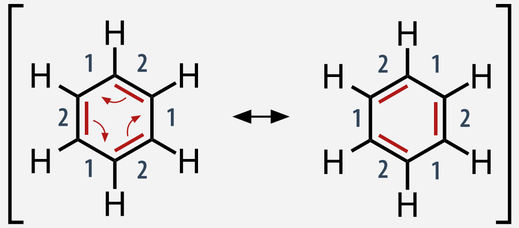
one neutral (major), twelve zwitterionic (minor) resonance structures

- **systems with more neutral resonance structures remain always more delocalized**

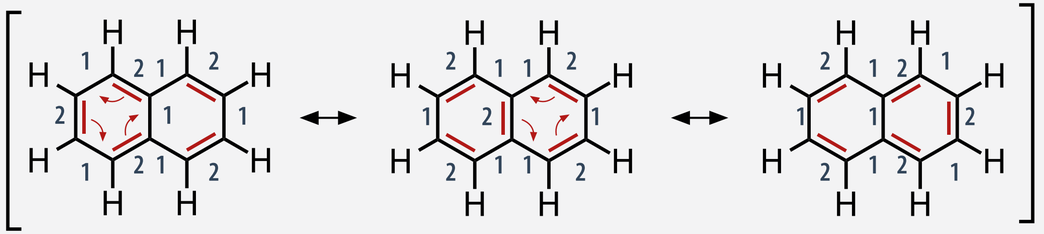
Resonance Structures as an Estimation for Bond Orders

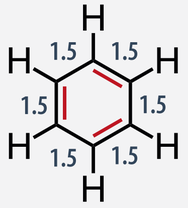
- ensemble of relevant resonance structures can be used as an approximation for bond orders

benzene

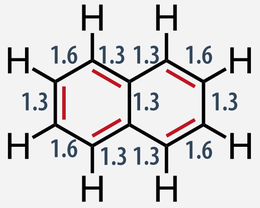


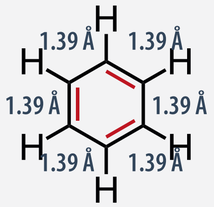
naphthalene



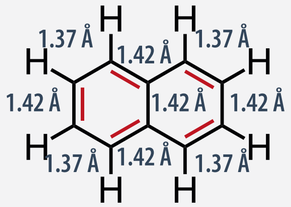


estimated bond orders





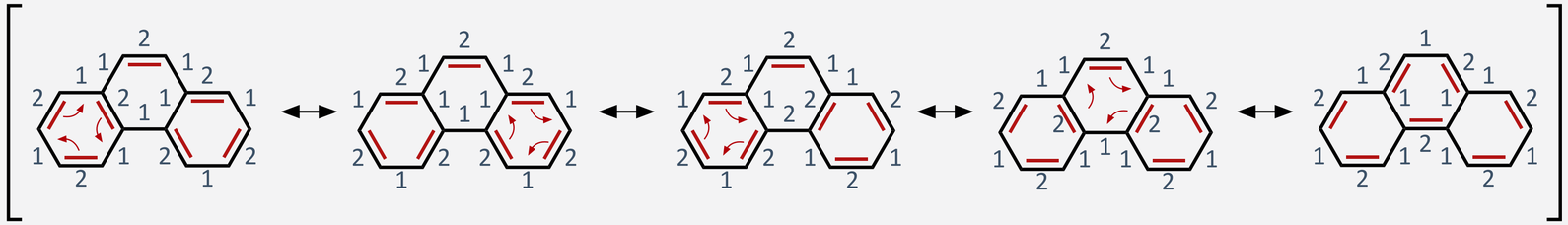
experimental bond lengths

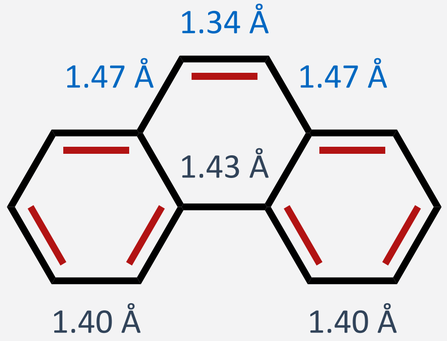


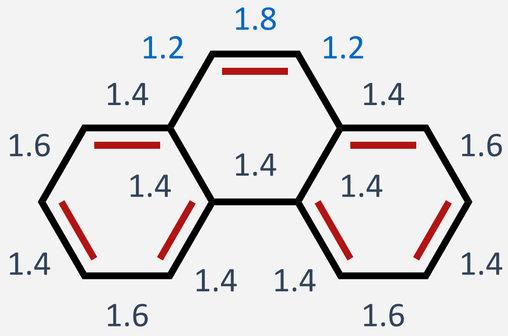
- determine all relevant resonance structures and individual bond orders in each structure
- **bond order of a given bond can be estimated from its average over all resonance structures**

Resonance Structures as an Estimation for Bond Orders

- ensemble of relevant resonance structures can be used as an approximation for bond orders





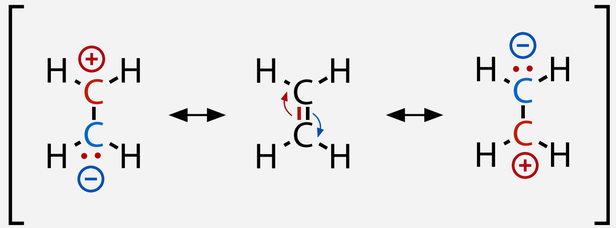


- determine all relevant resonance structures and individual bond orders in each structure
- **bond order of a given bond can be estimated from its average over all resonance structures**

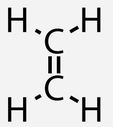
Resonance Structures Involving Electron-Withdrawing Groups

- multiple bonds to electronegative heteroatoms (O, N, S) that are part of the π-system

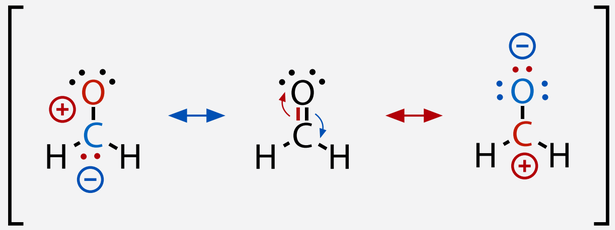
ethene



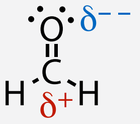
minor major minor



formaldehyde



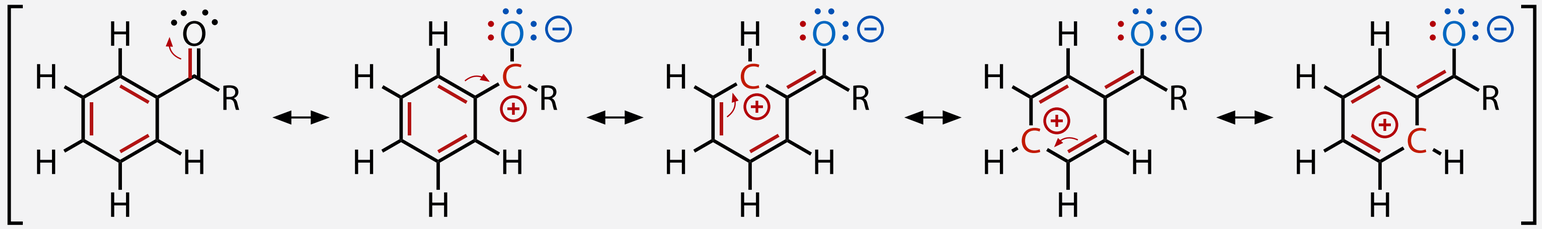
negligible major major

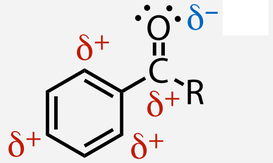


- negative formal charge on electronegative heteroatoms significantly better stabilized
- contrary to all-carbon systems, this results in molecule with strong dipole moment
- **multiple bonds to electronegative heteroatoms are electron-withdrawing "–M substituents"**

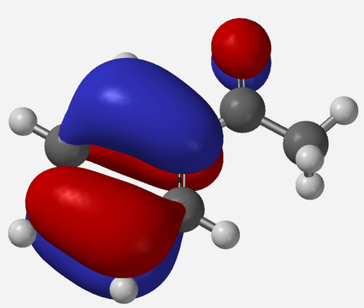
Resonance Structures Involving Electron-Withdrawing Groups

- –M substituents determine electron density and reactivity patterns in π-conjugated systems

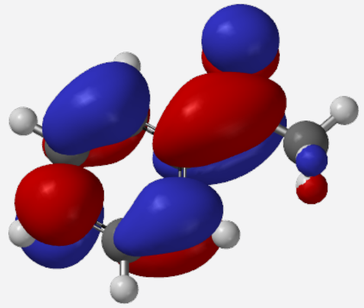




charge distribution



HOMO



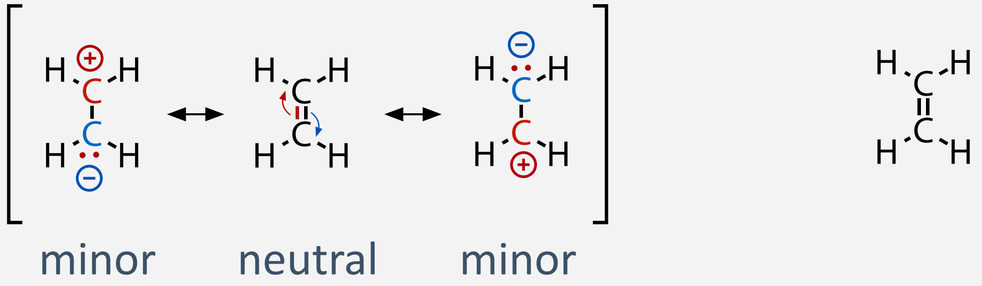
LUMO

- overall electron density in the π-system decreased (compared to benzene)
- every second carbon in the π system carries positive formal charge in resonance structures
- every second carbon in delocalized π system is electron-poor (positive partial charge δ+)

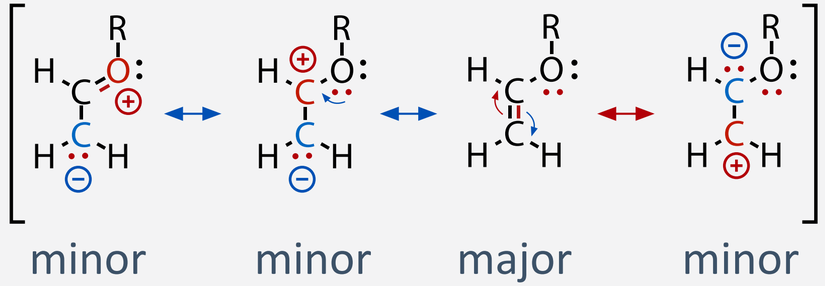
Resonance Structures Involving Electron-Donating Groups

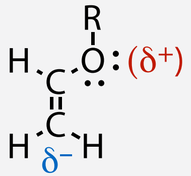
- atoms with free electron pairs (O, N, S, Hal) single-bonded to the π system

ethene



alkoxy ethene

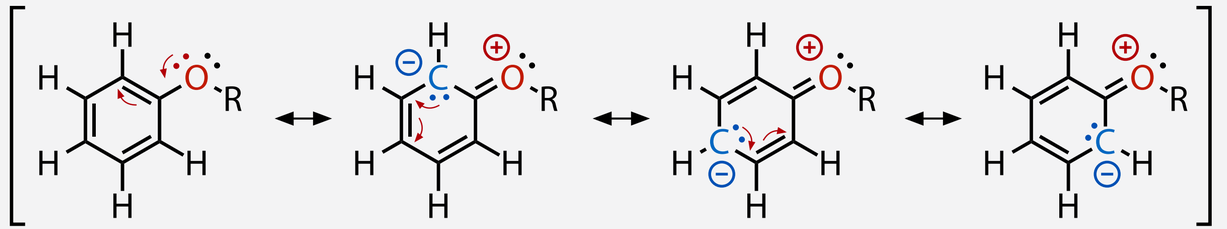


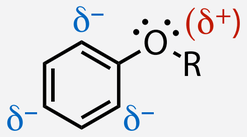


- positive formal charge on electronegative heteroatoms, but still electron octet!
- contrary to all-carbon systems, this results in molecule with strong dipole moment
- **atoms with free electron pairs are electron-donating “+M substituents”**

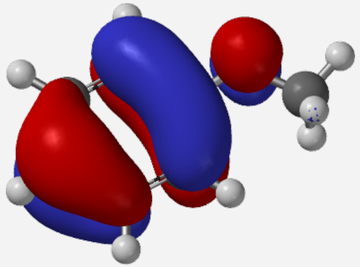
Resonance Structures Involving Electron-Donating Groups

- +M substituents determine electron density and reactivity patterns in π-conjugated systems

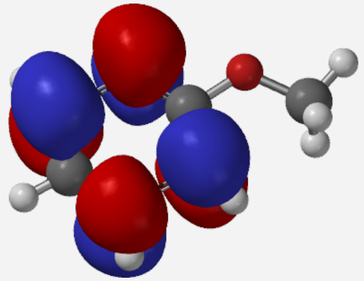




charge distribution



HOMO



LUMO

- overall electron density in the π-system increased (compared to benzene)
- every second carbon in the π system carries negative formal charge in resonance structures
- every other carbon in delocalized π system is electron-rich (negative partial charge δ–)

Learning Outcomes

- **conjugated multiple bonds interact, and electrons are delocalized**
- **double bonds have bond order <2, single bonds have bond order >1**
- **π-orbitals extend over all carbons and “do not look like” double bond MO**
- **electron delocalization particularly pronounced for “aromatic” systems**
- **delocalization can be represented by resonance structures**
  - neutral resonance structures strongly preferred over zwitterionic ones
  - number of resonance structures represents degree of delocalization
  - average over all resonance structures allows to estimate bond order
  - –M substituents decrease electron density, create positive partial charges
  - +M substituents increase electron density, create negative partial charges