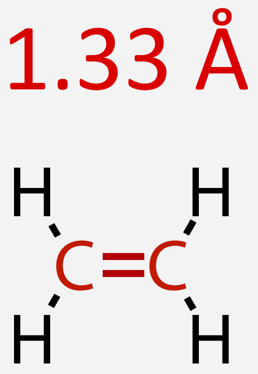
2.5 Electron Delocalization and Resonance Structures

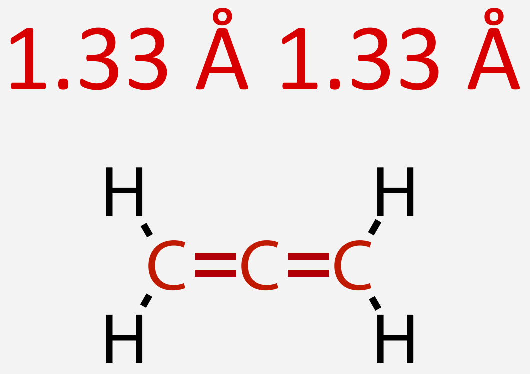
Reading Recommendations

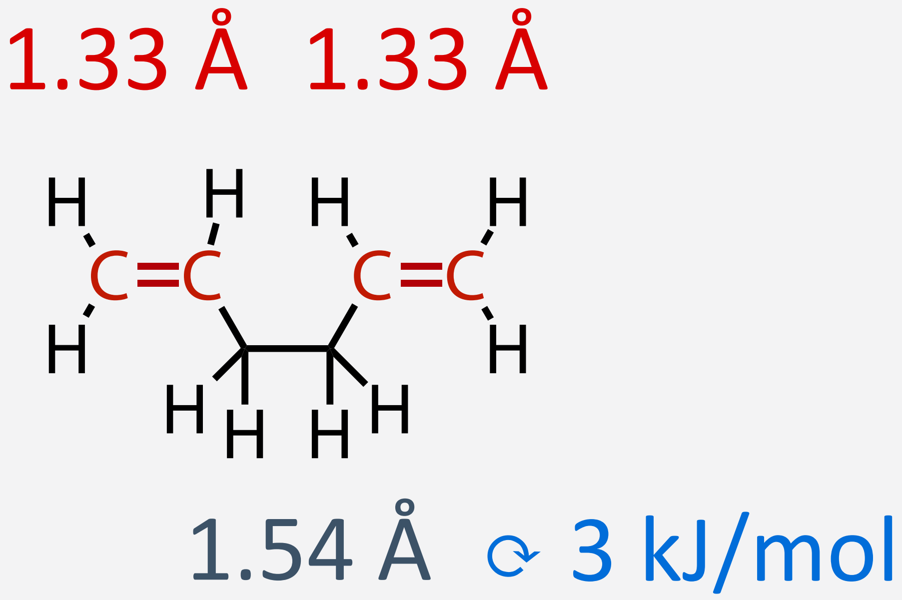
- Clayden, Greeves, Warren, *Organic Chemistry*, Oxford University Press, 2nd ed., **2012**, *pp* 141–162.
- Jamart, Bodiguel, Brosse, *Les cours de Paul Arnaud - Cours de chimie organique*, Dunod, 19th ed., **2015**, *pp* 87–97.

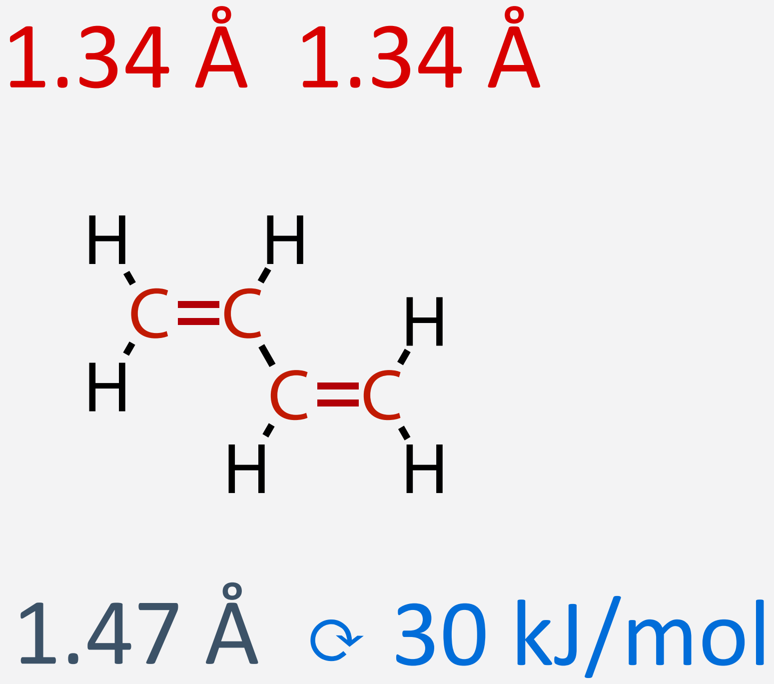
Molecules with Several Multiple Bonds

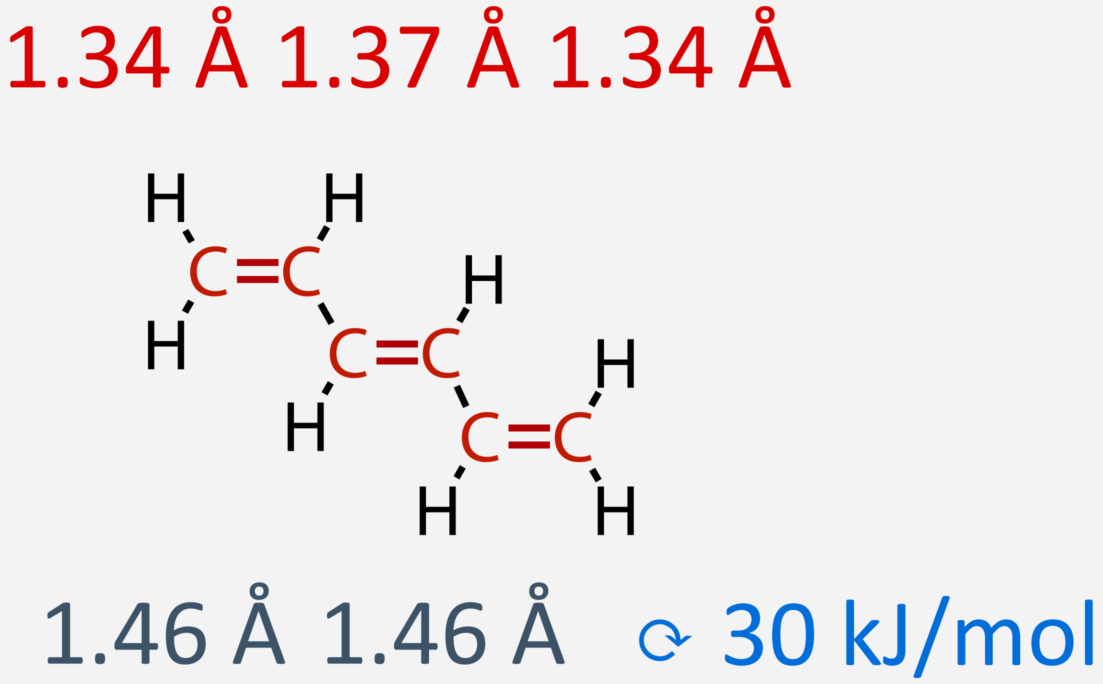
- bond lengths for single and double bonds, energy barriers for rotation for single bonds

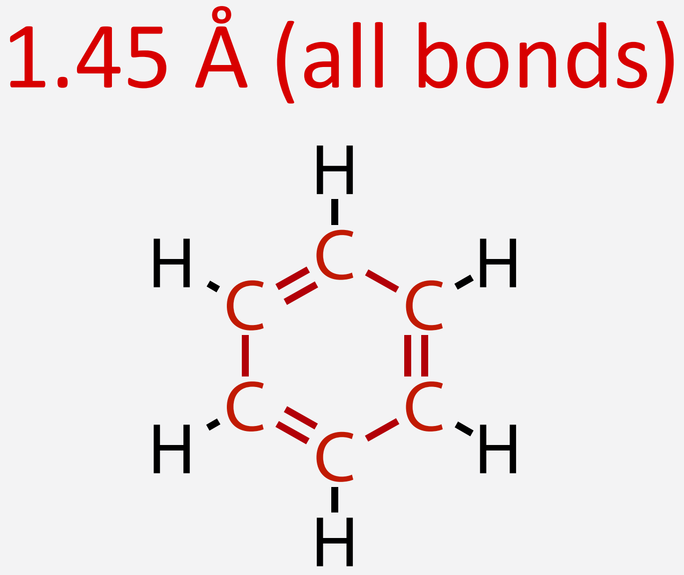








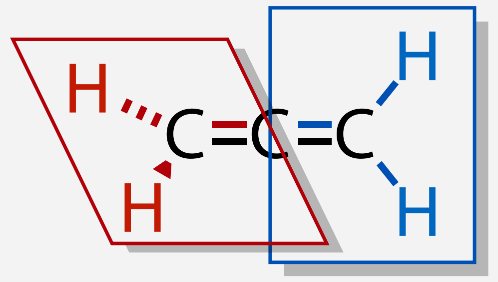




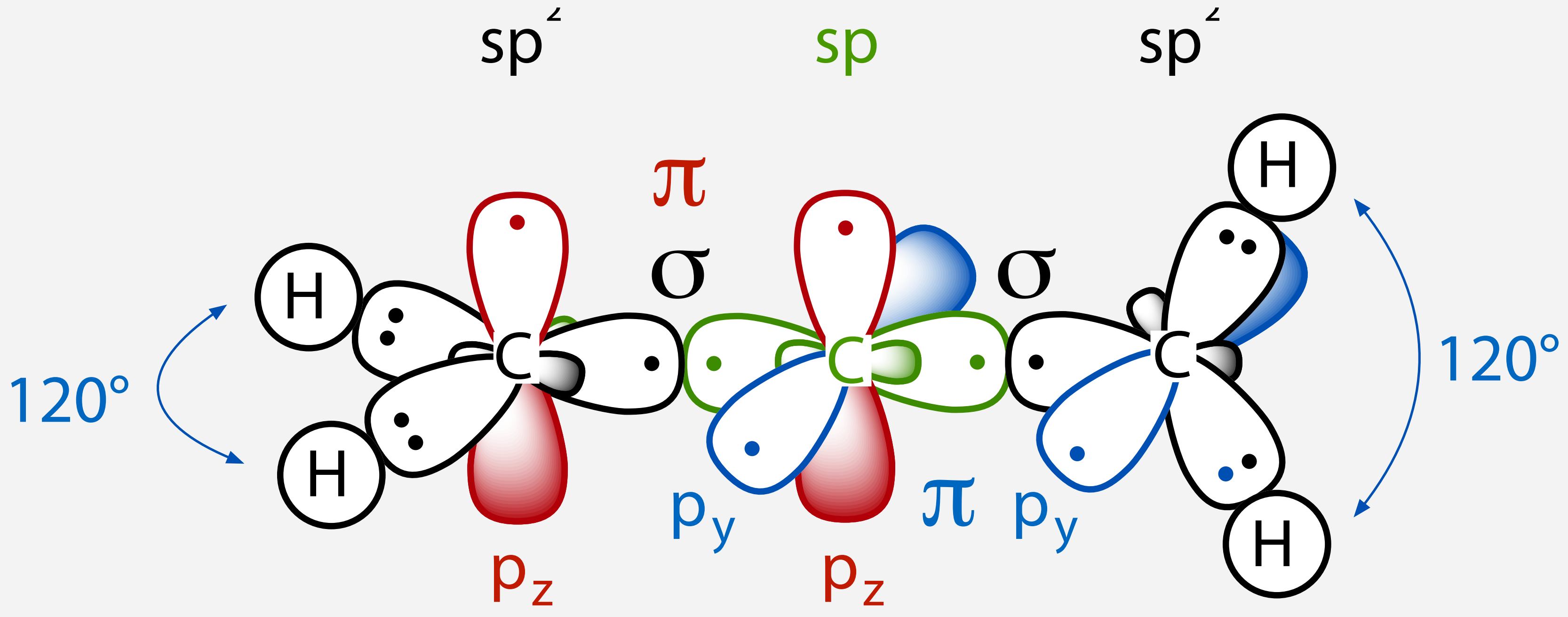
- **alternating double and single bonds are called conjugated double bonds**
- **conjugated double bonds are longer than normal**
- **single bonds between conjugated double bonds are shorter and have a high rotation barrier**

Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

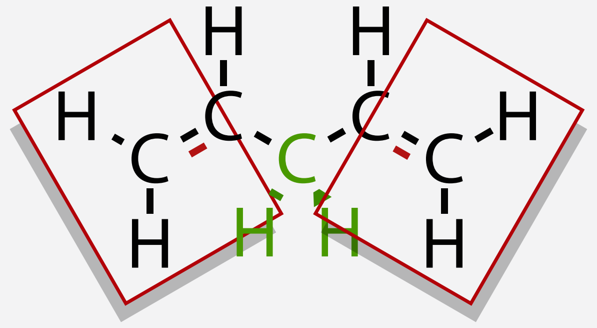
- “cumulated double bonds” are in orthogonal planes, do not interact electronically



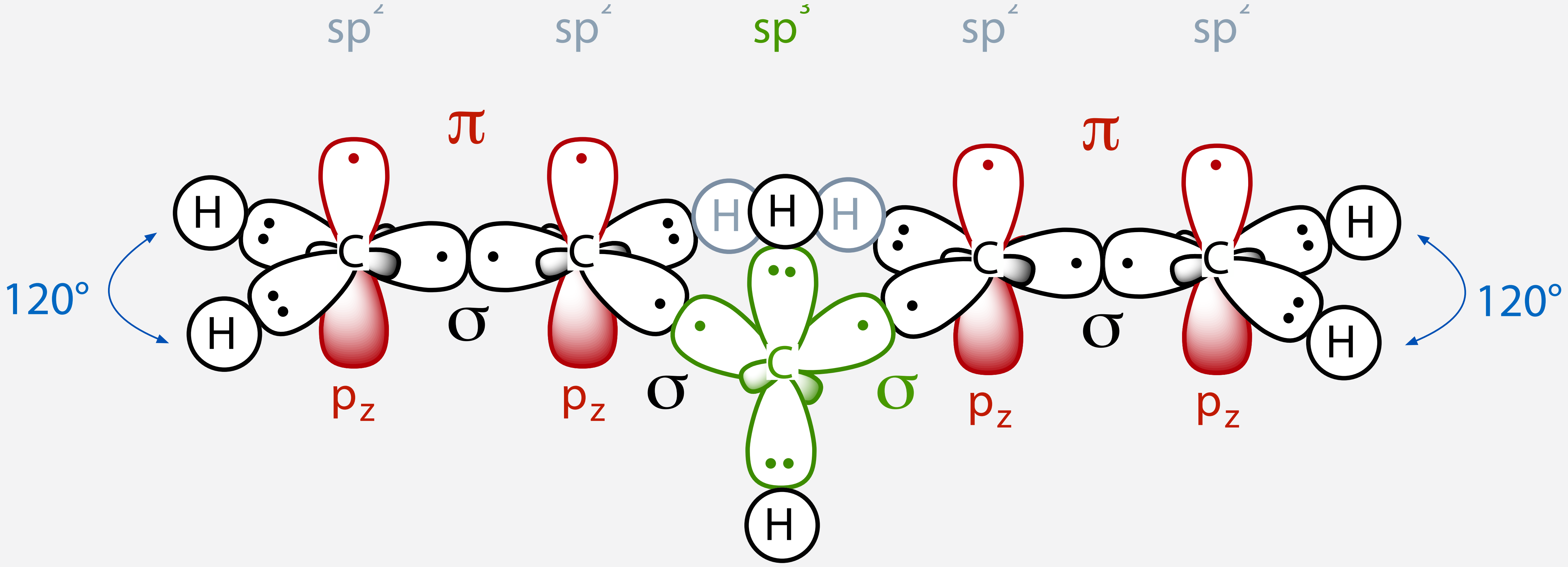
1,2-propadiene



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



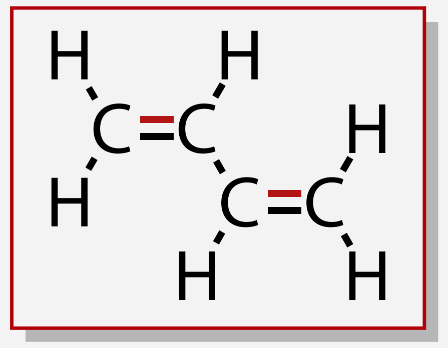
1,5-pentadiene



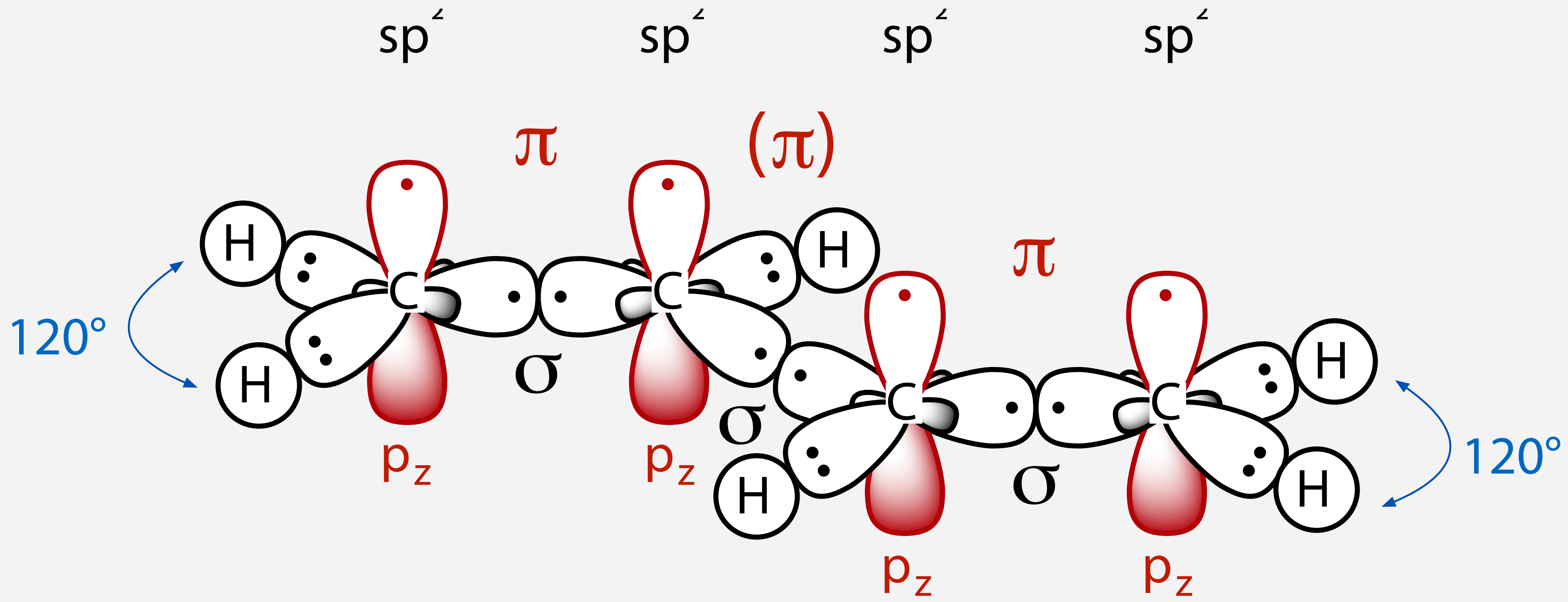
- **neither cumulated nor isolated multiple bonds “communicate”, i.e., interact electronically**

Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

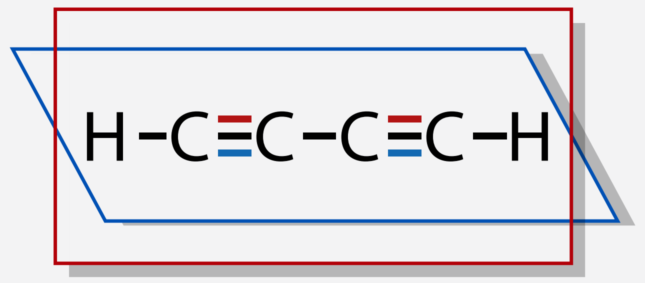
- “conjugated double bonds” are in the same plane and p_z orbitals are in direct contact



1,3-butadiene

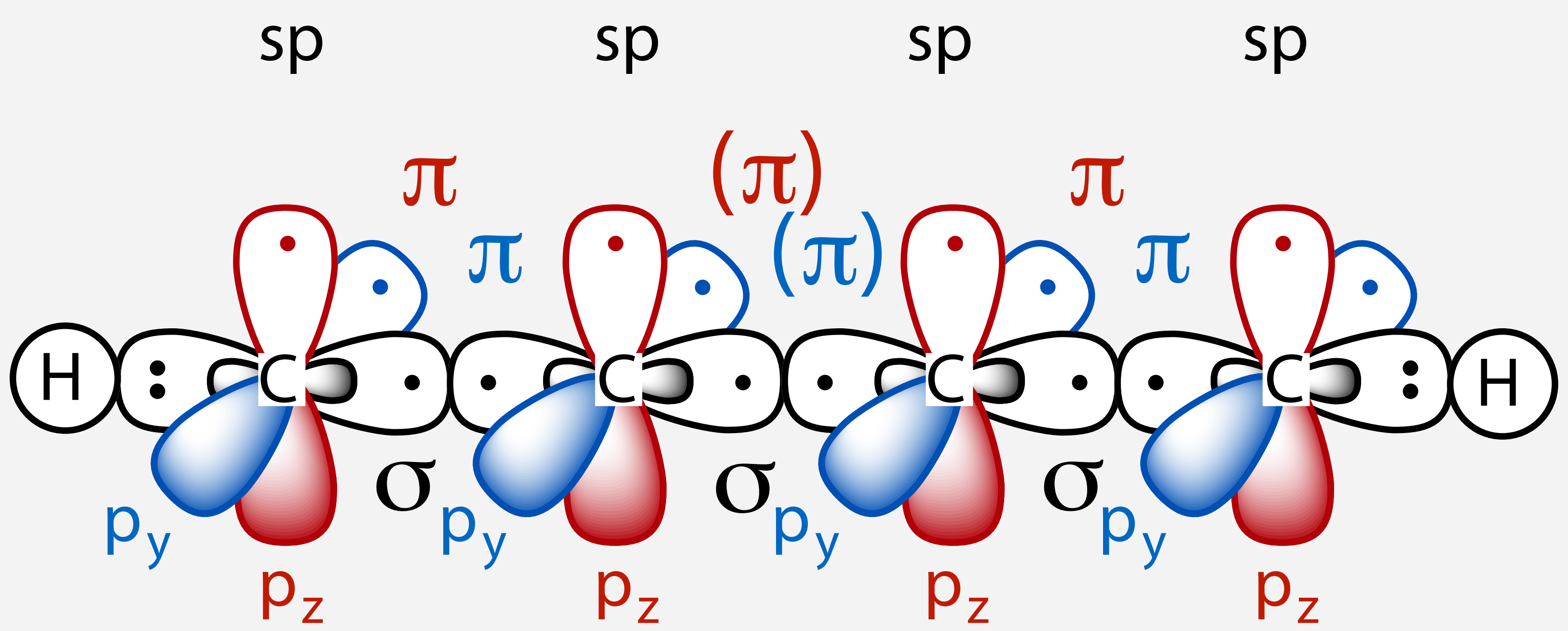


- “conjugated triple bonds” are in the same planes, pz and py orbitals are in direct contact



$H-C\equiv C-C\equiv C-H$

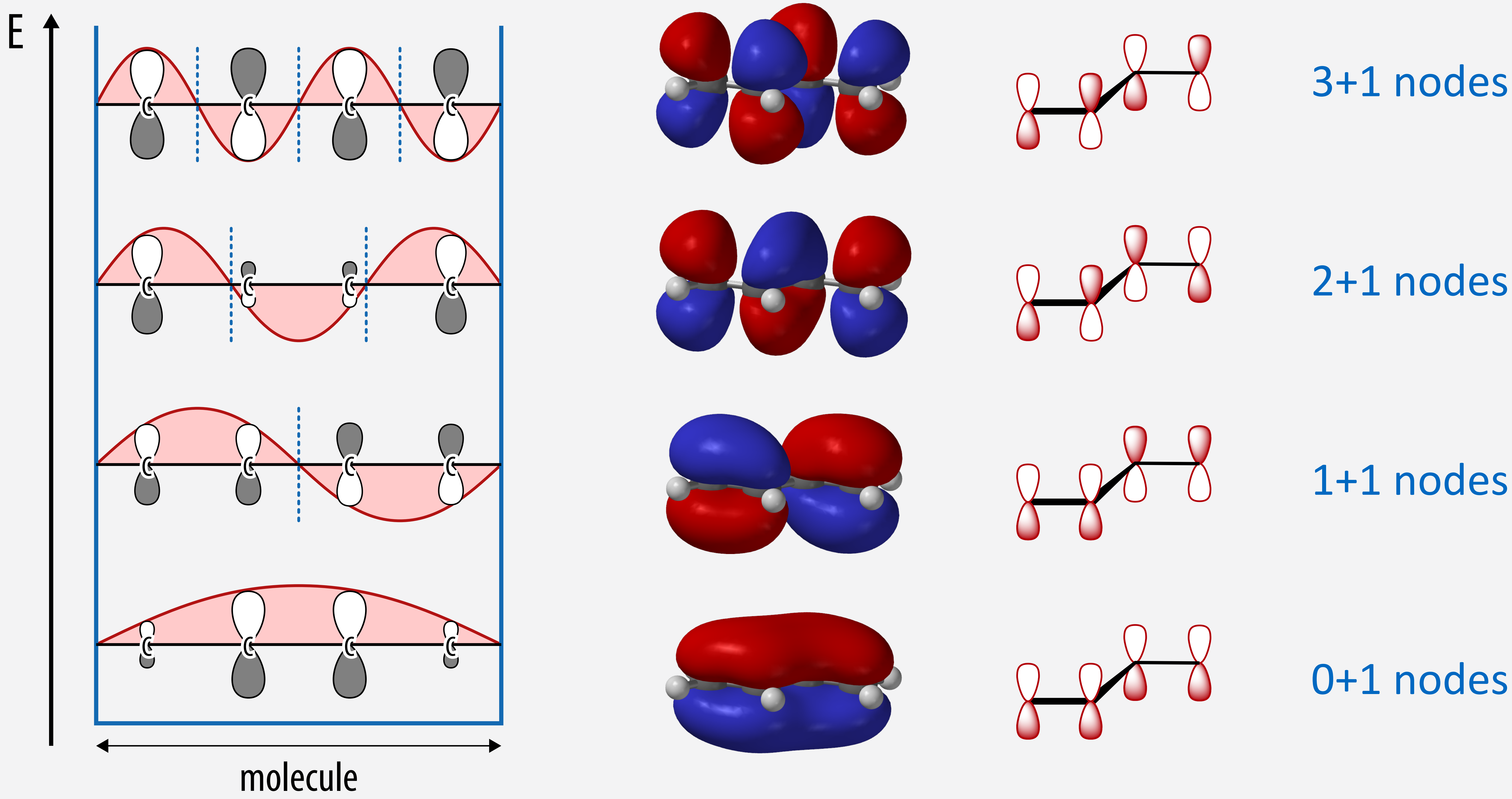
1,3-butadiyne



- **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

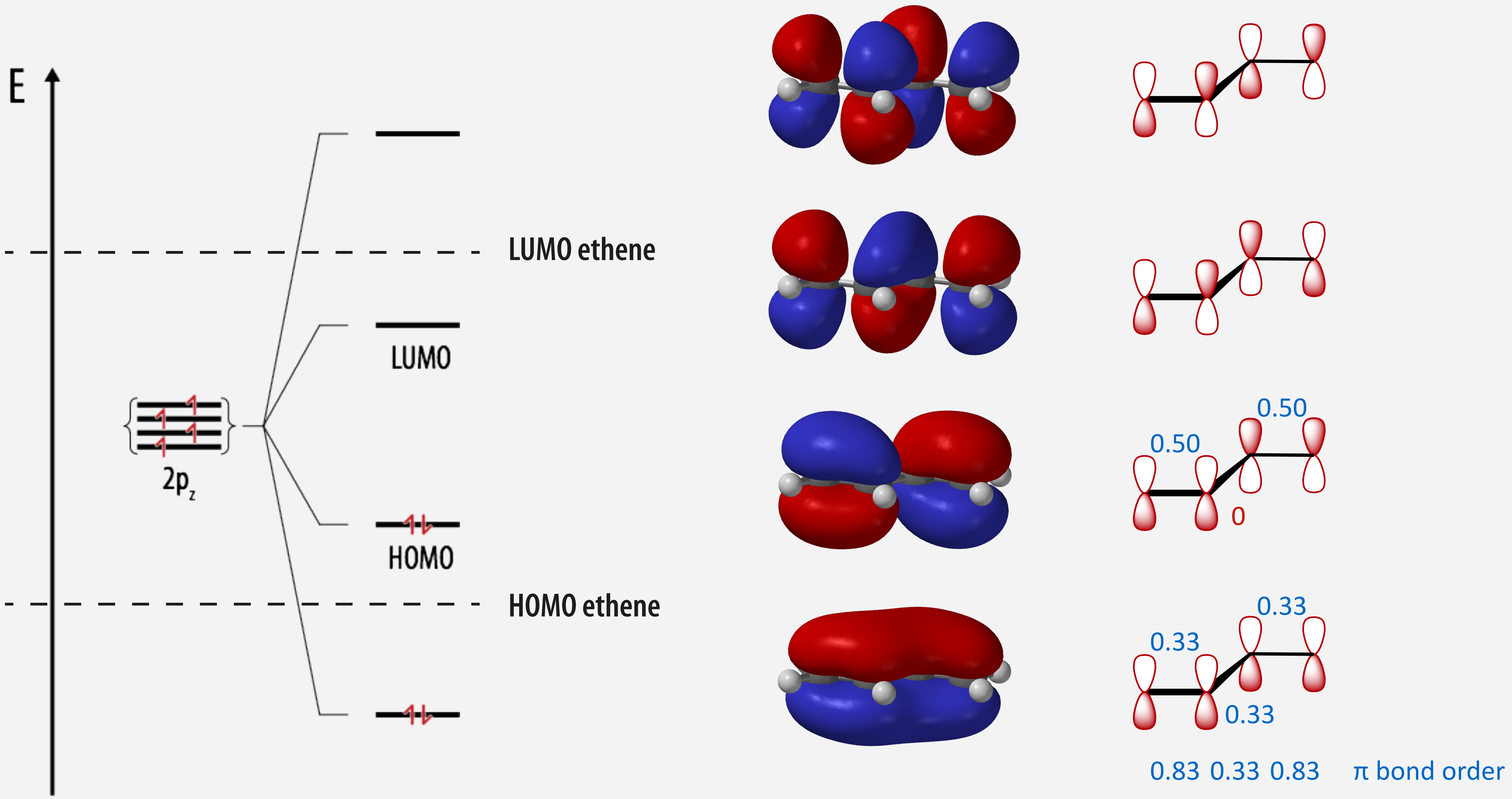
- “electron in 1D Box with infinite potential well” is a model for linear π-conjugated systems



- **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**

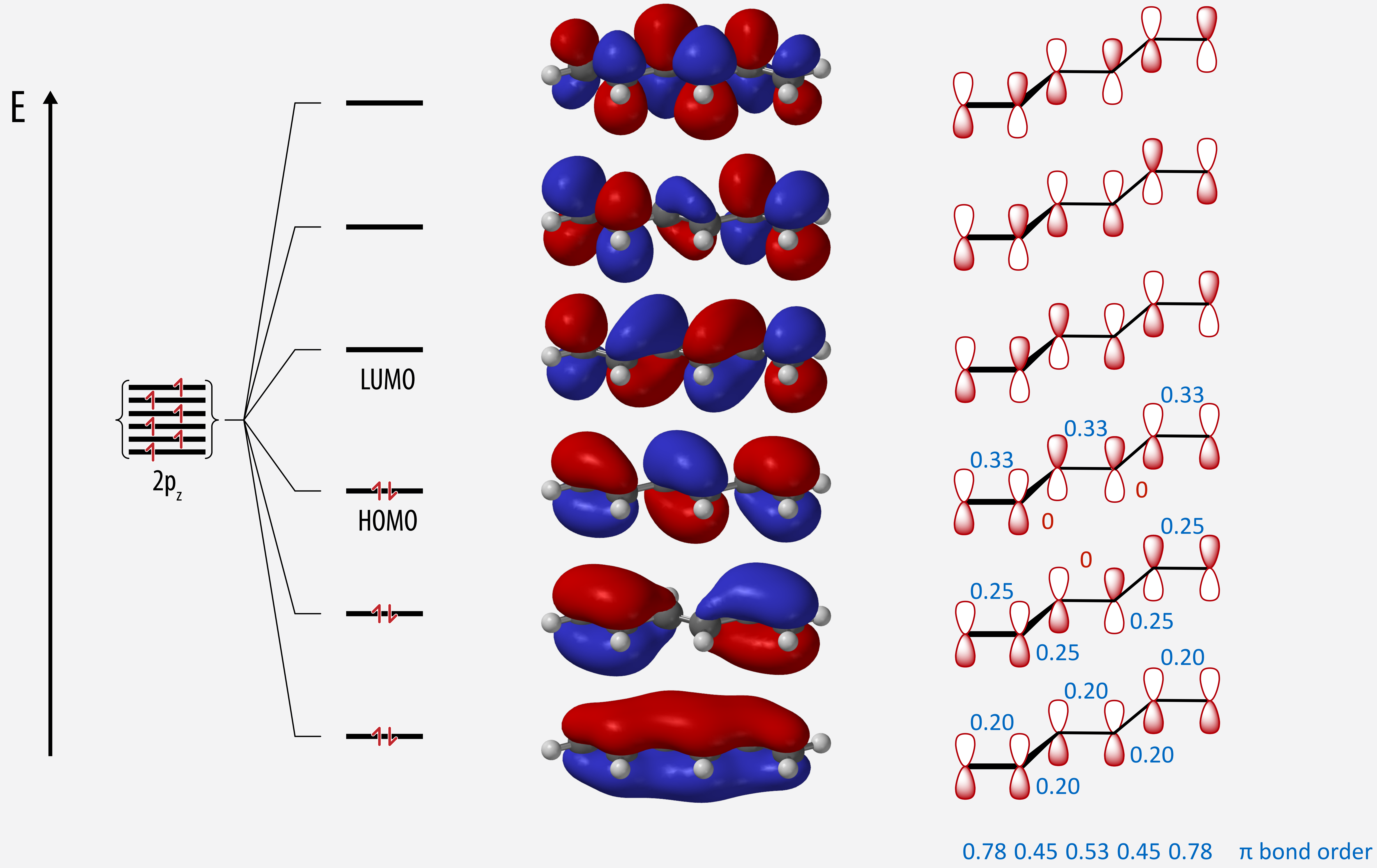
Frontier Orbitals and Bond Orders in 1,3-Butadiene

- 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”**

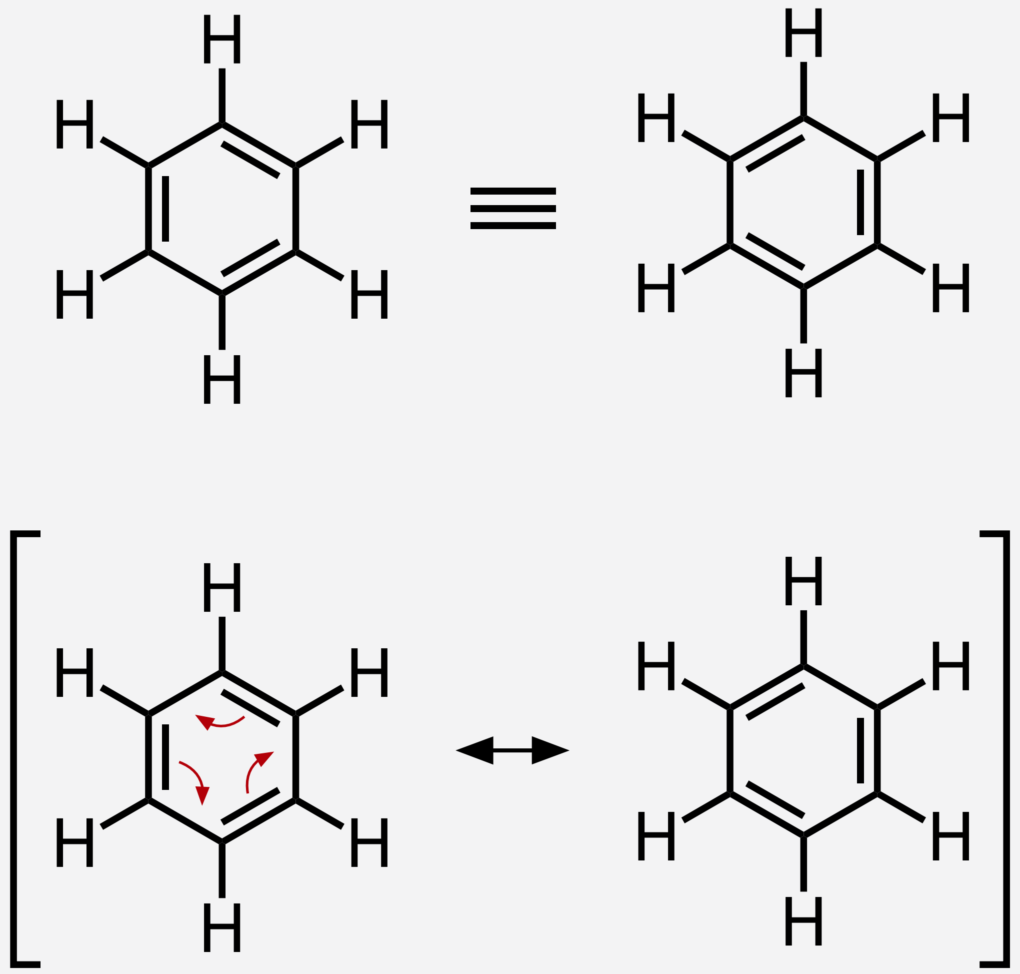
Frontier Orbitals and Bond Orders in 1,3,5-Hexatriene

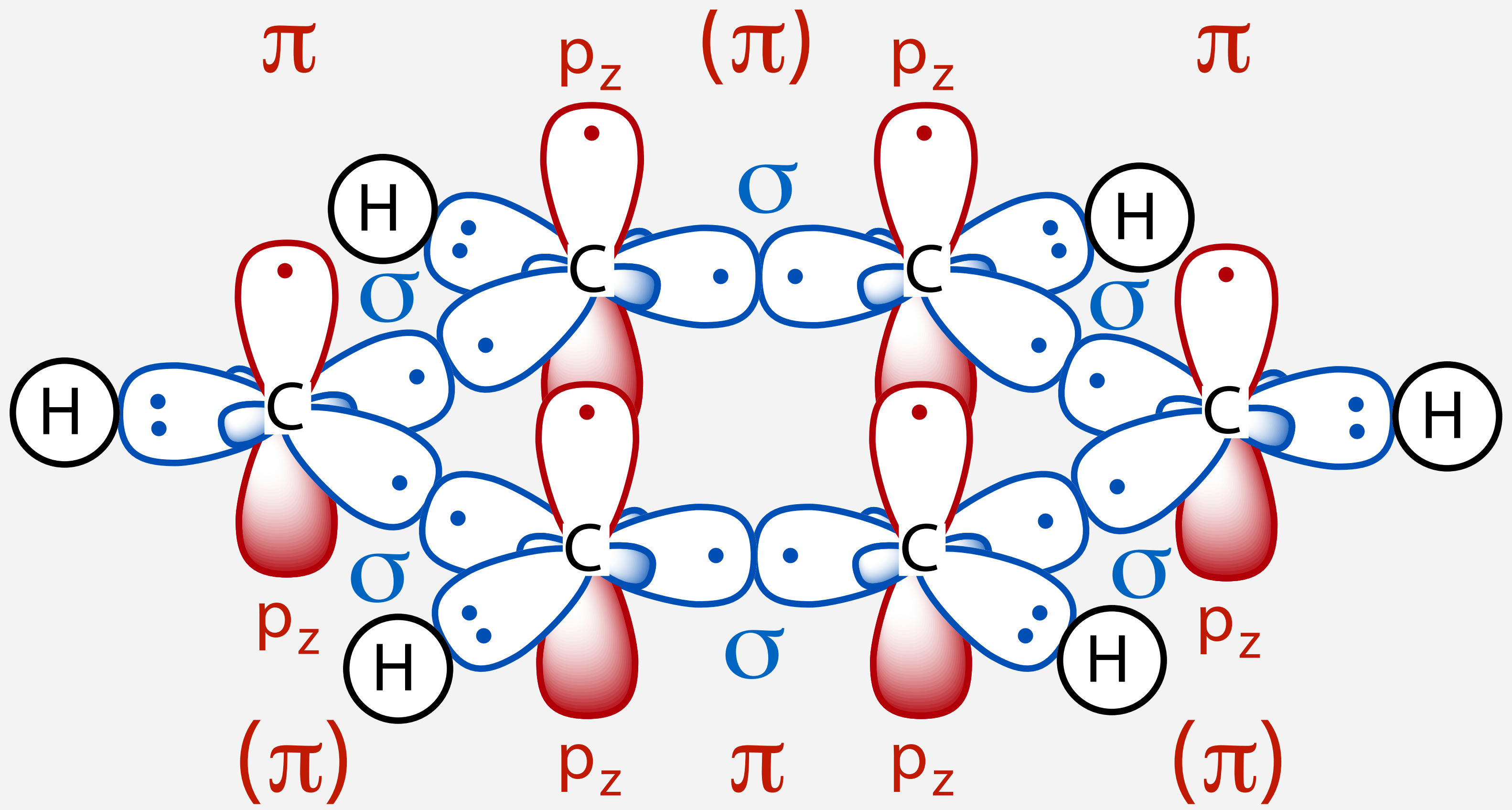


- **all π-electrons delocalized over entire molecule**
- **HOMO/LUMO gap decreases, bond order of bonds converges to 1.5**

Electron Delocalization in Cyclic π-Conjugated Multiple Bonds

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

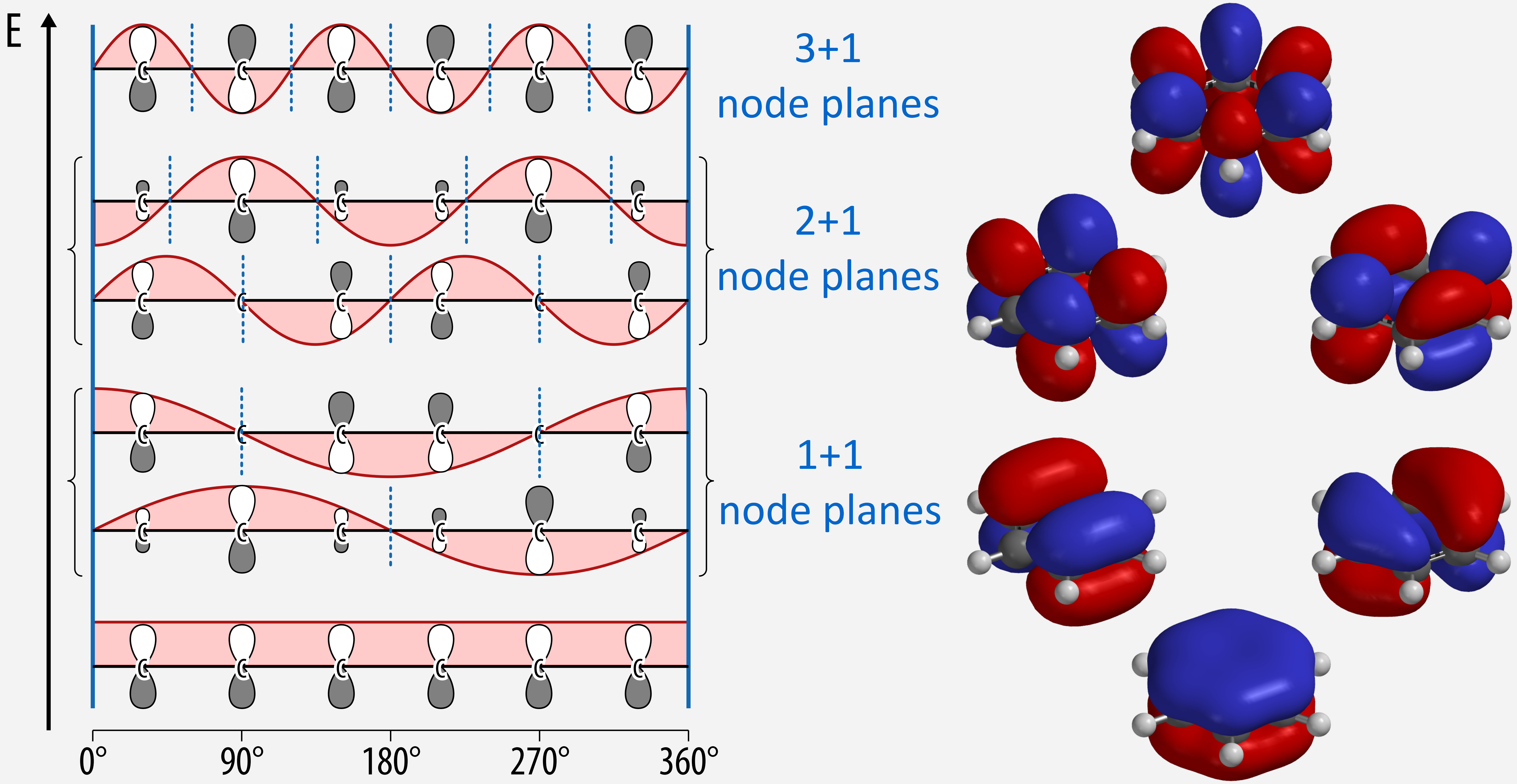




- **cyclic conjugated double bonds can be represented by (neutral) resonance structures**
- **all bonds are symmetrically equivalent, equal bond length 1.45 Å, bond order 1.5**
- **“aromatic” compounds with 2n+1 cyclic conjugated double bonds are particularly stable**

“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



3+1
node planes

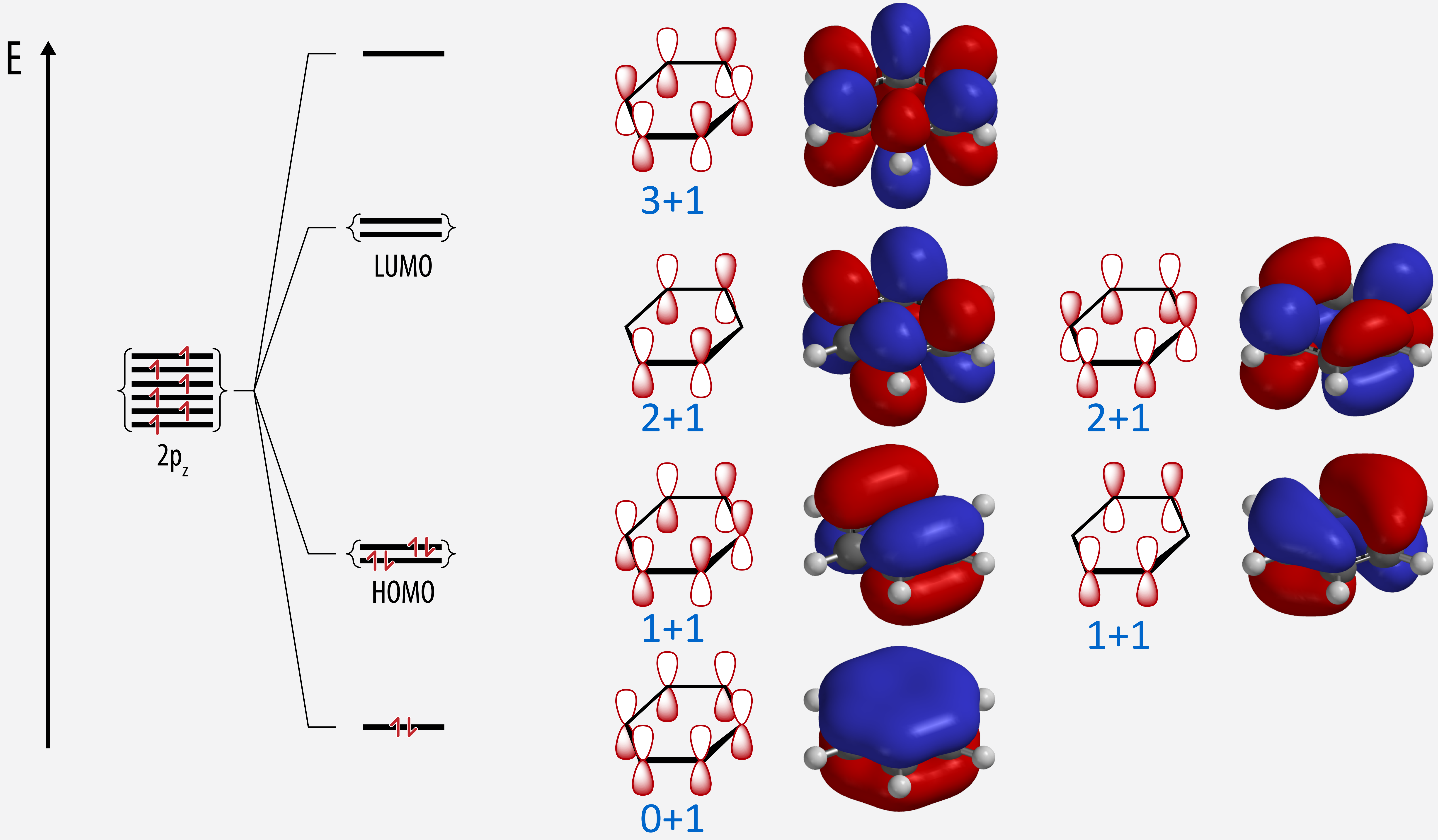
2+1
node planes

1+1
node planes

- **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

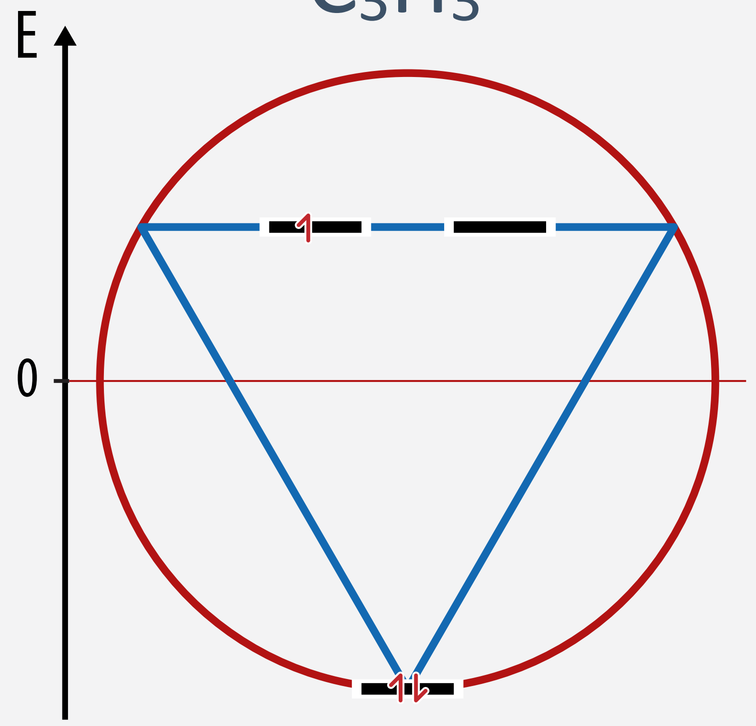
- “electron in a box with steady boundary condition” is a model for cyclic π-conjugated systems



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

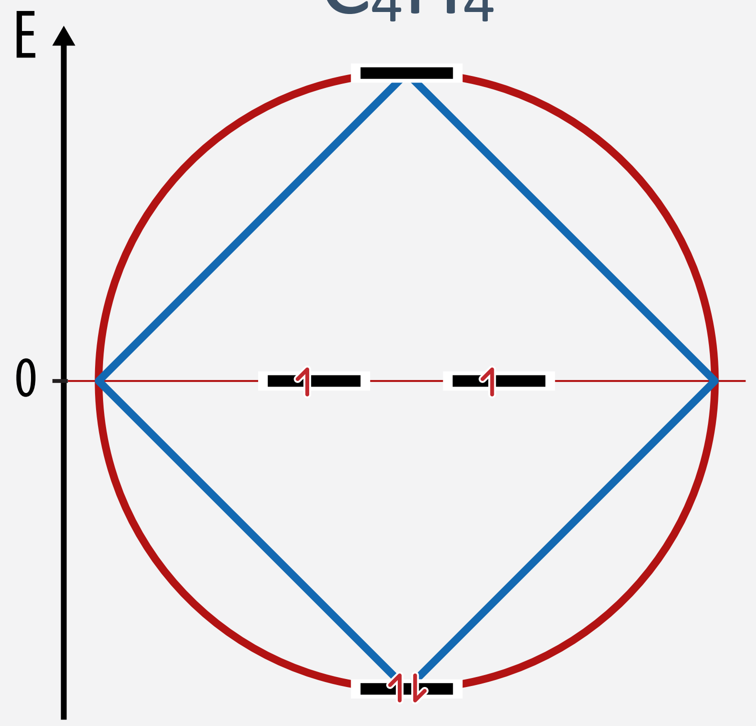
Approximation for the MO Energy Diagrams of Cyclic π-Conjugated Systems

$C_3H_3^\bullet$



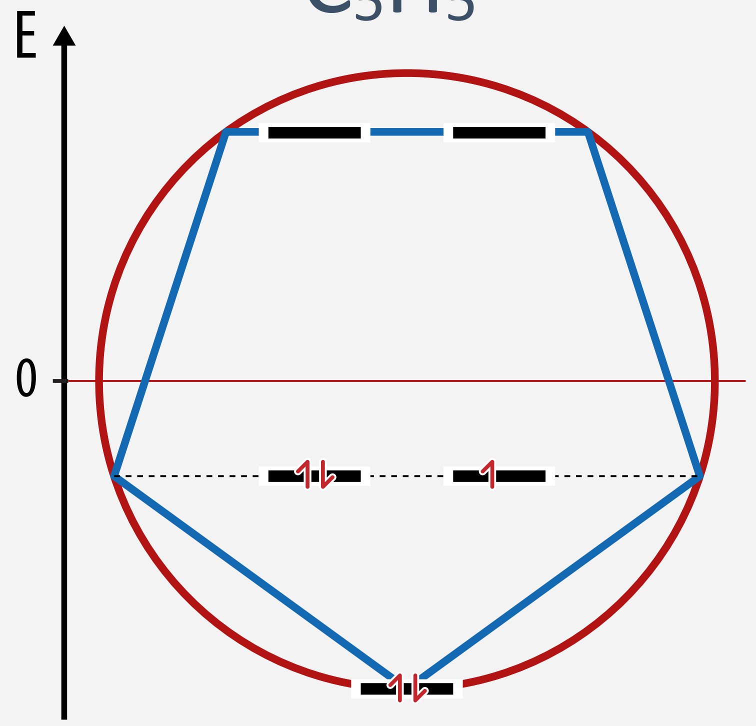
very unstable
open shell, destabilized

C_4H_4



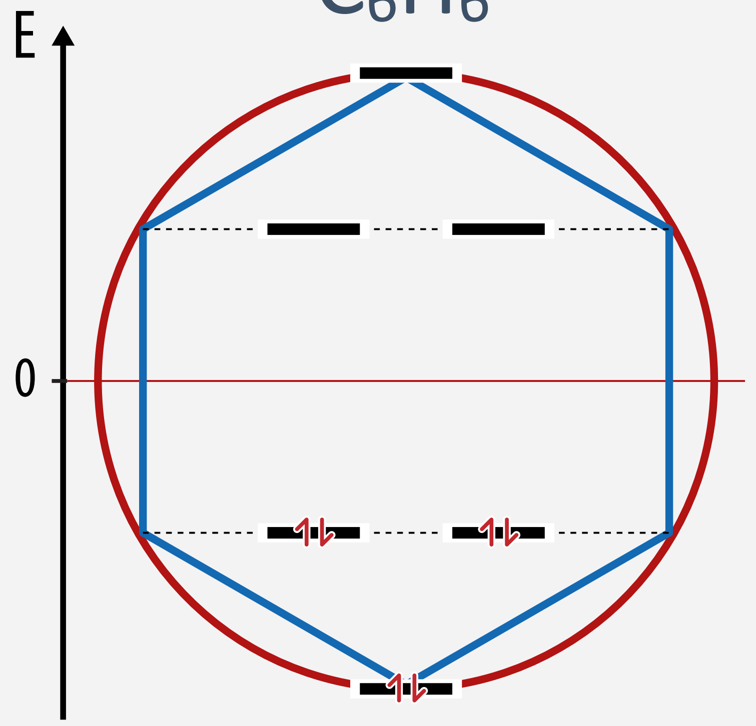
very unstable
open shell, destabilized

$C_5H_5^\bullet$



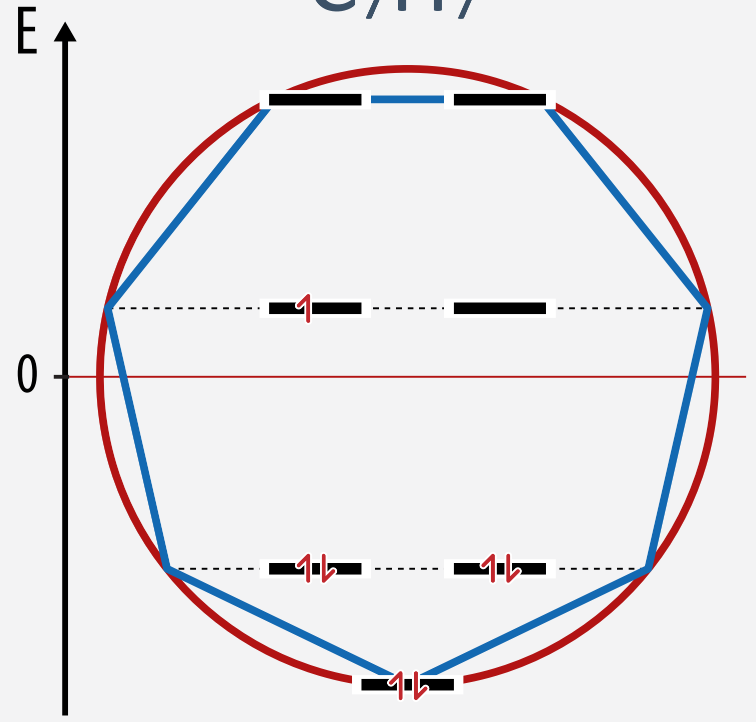
unstable
open shell, stabilized

C_6H_6



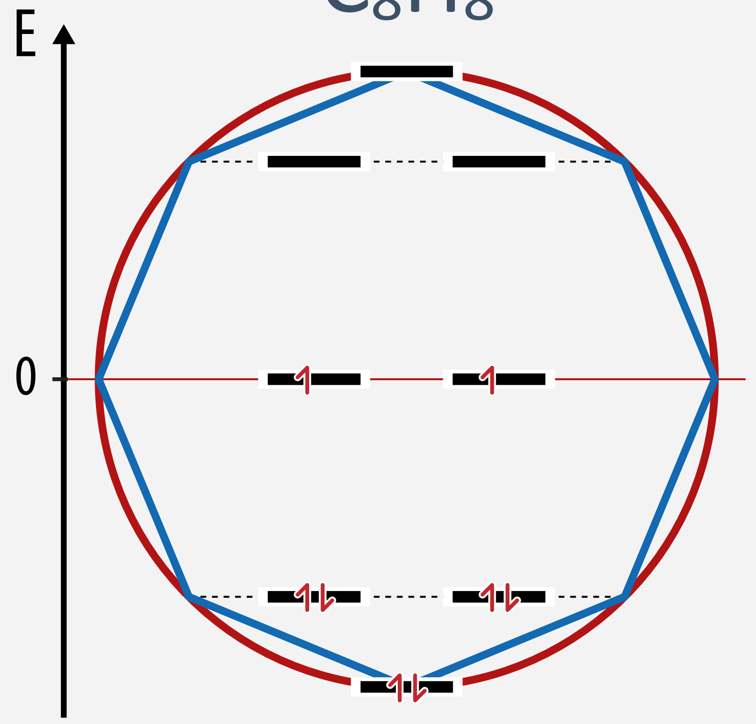
very stable
closed shell, stabilized

$C_7H_7^\bullet$



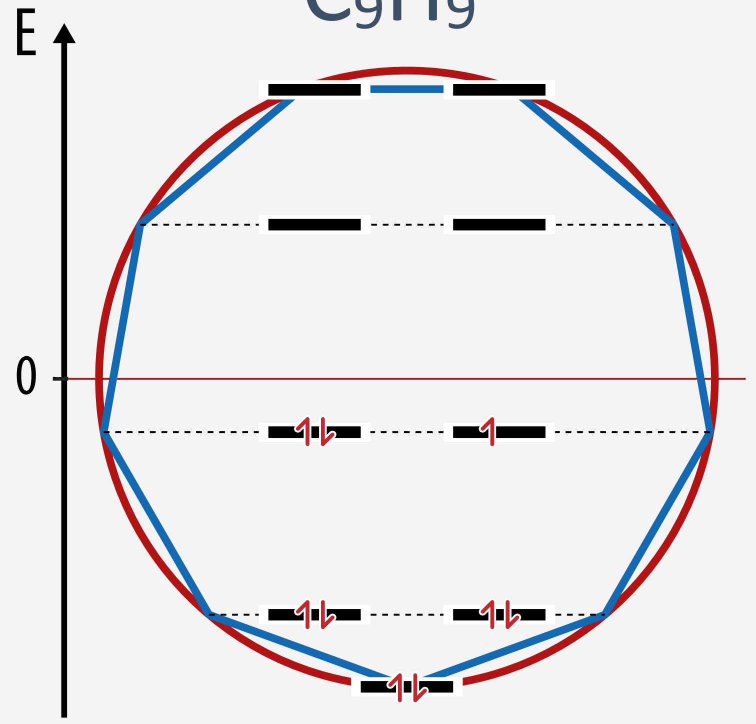
very unstable
open shell, destabilized

C_8H_8



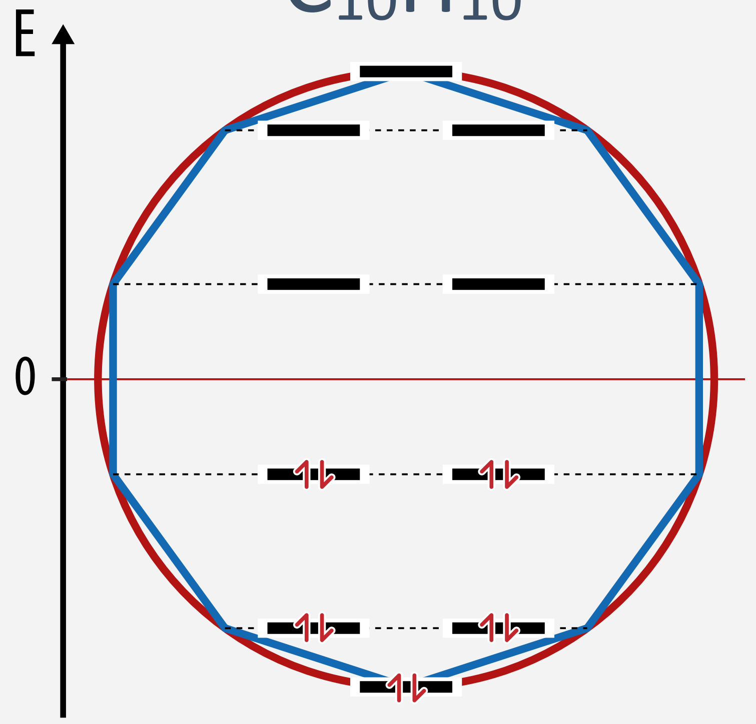
very unstable
open shell, destabilized

$C_9H_9^\bullet$



unstable
open shell, stabilized

$C_{10}H_{10}$



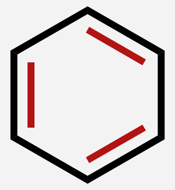
very stable
closed shell, stabilized

- **origin of the Hückel rule for "aromaticity": monocyclic systems with 4*n*+2 electrons are very stable**

Examples of Aromaticity and Aromatic Compounds

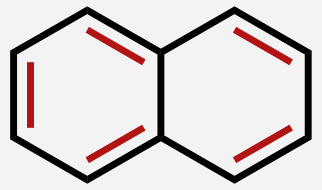
- “aromaticity” is a historically derived concept to describe “unusual” chemical stability

benzene



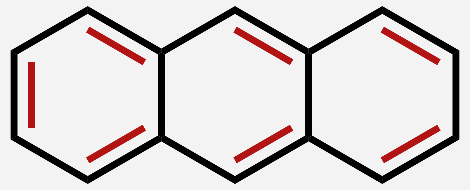
6π

naphthalene



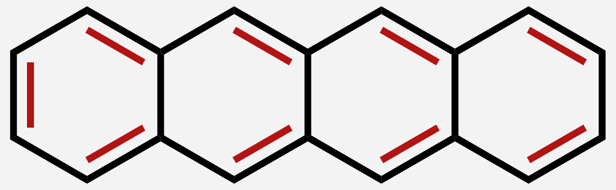
10π

anthracene



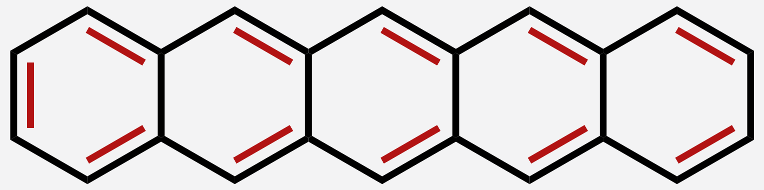
14π

tetracene



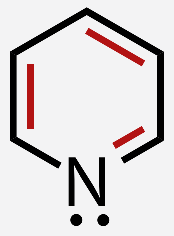
18π

pentacene



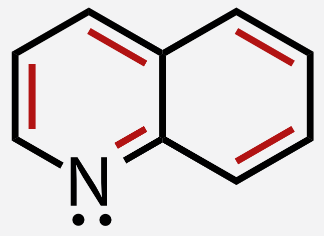
22π

pyridine



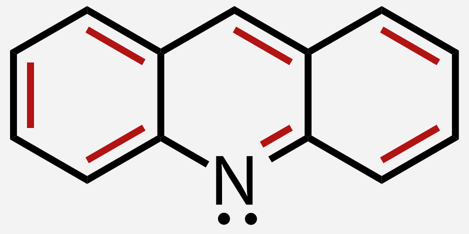
6π

quinoline



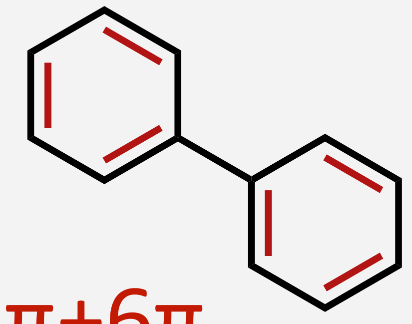
10π

acridine



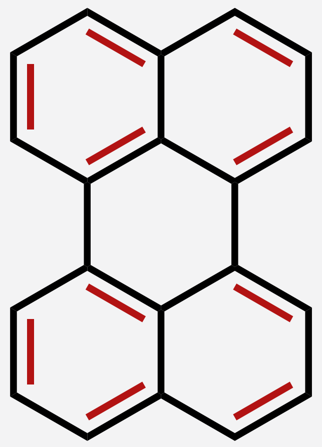
14π

biphenyl



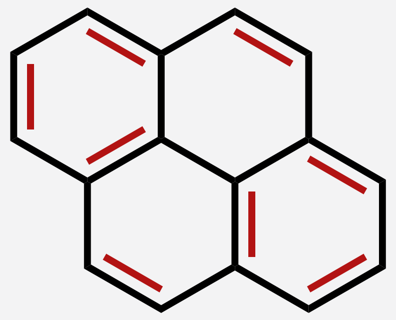
6π+6π

perylene



10π+10π

pyrene

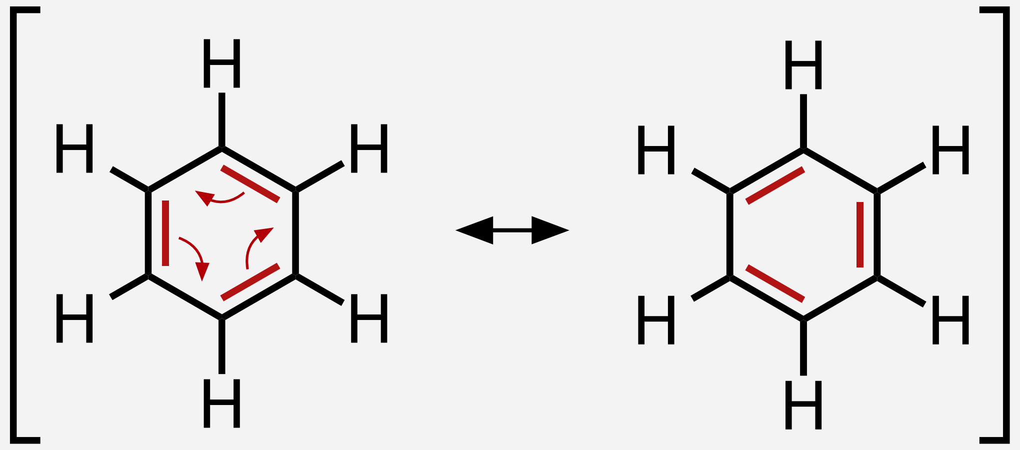


16π

- **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**



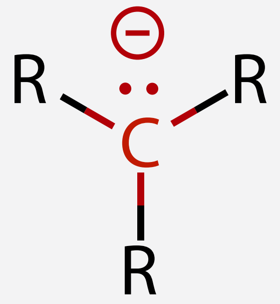
- **drawing the neutral resonance structures of cyclic π-conjugated systems:**
    - draw σ bond framework of sp^2-hybridized carbons/heteroatoms (and attached atoms)
    - draw the π electron pairs of the double bonds (ideally in another color)
    - indicate with arrows how to flip π electron pair 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

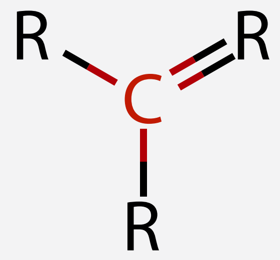
- **resonance structures are just representations of delocalization**

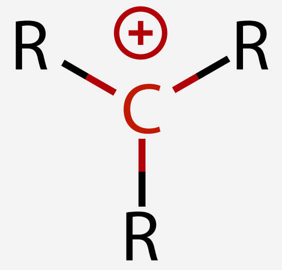
- **π electrons do not really move/resonate**

Representing Delocalization with Resonance Structures

- zwitterionic resonance structures comprise positive/negative formal charges





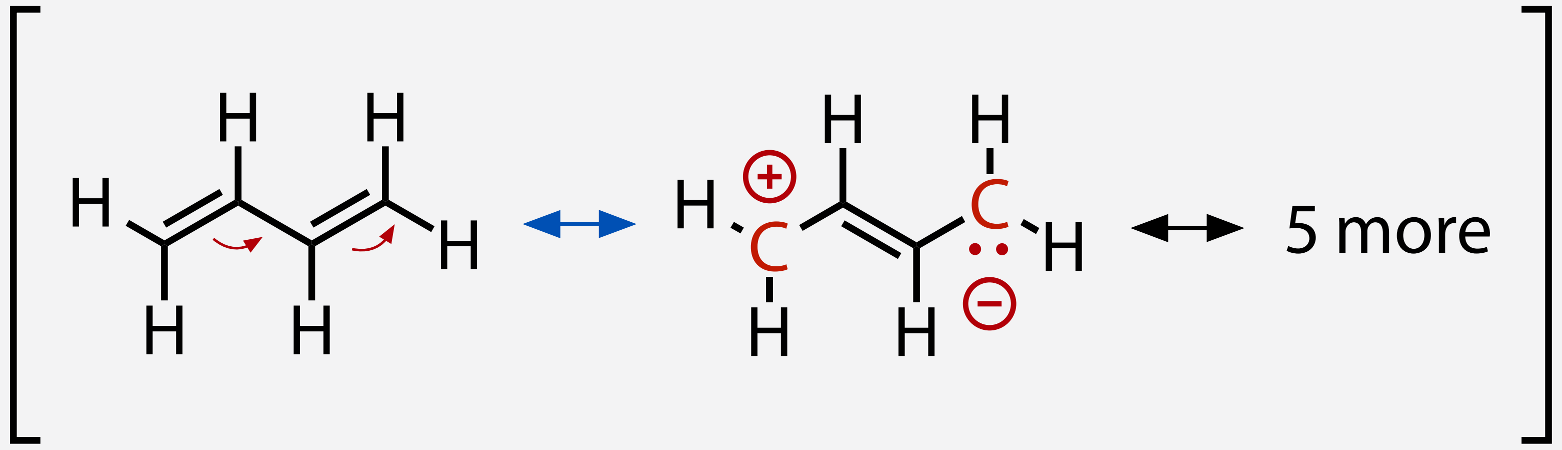


carbanion	**double-bonded carbon**	**carbocation**
trivalent	tetravalent	trivalent
5 electrons negative formal charge	4 electrons neutral	3 electrons positive formal charge
3 bonds, 1 electron pair octet rule fulfilled	4 bonds octet rule fulfilled	3 bonds electron sextet (deficient)

- **formal charges are determined by homolytic bond cleavage and counting electrons**
- **valency determined by counting electron pairs involved in covalent bonds to other atoms**

Representing Delocalization with Resonance Structures

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

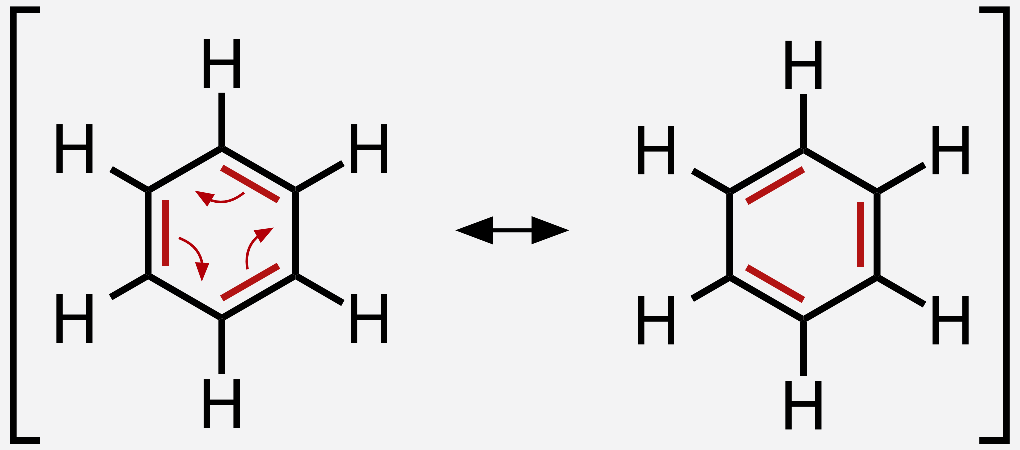


- **drawing the zwitterionic resonance structures of linear π-conjugated systems:**
  - draw σ bond framework of sp^2-hybridized carbons/heteroatoms (and attached atoms)
  - draw the π electron pairs of the double bonds (ideally in another color)
  - indicate with arrows how to flip π electron pair to 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

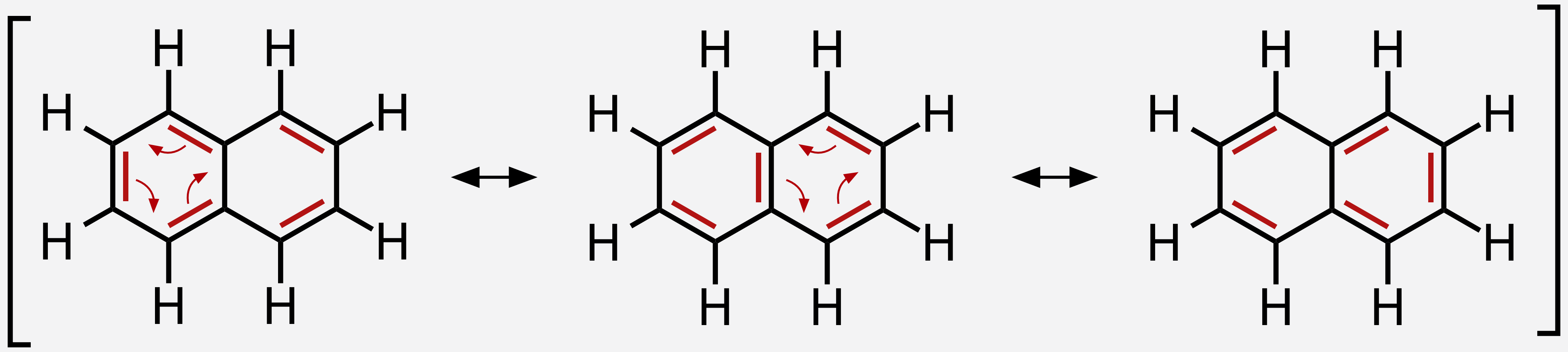
- **degree of delocalization can be estimated from total number of resonance structures**

benzene



two neutral resonance structures

naphthalene



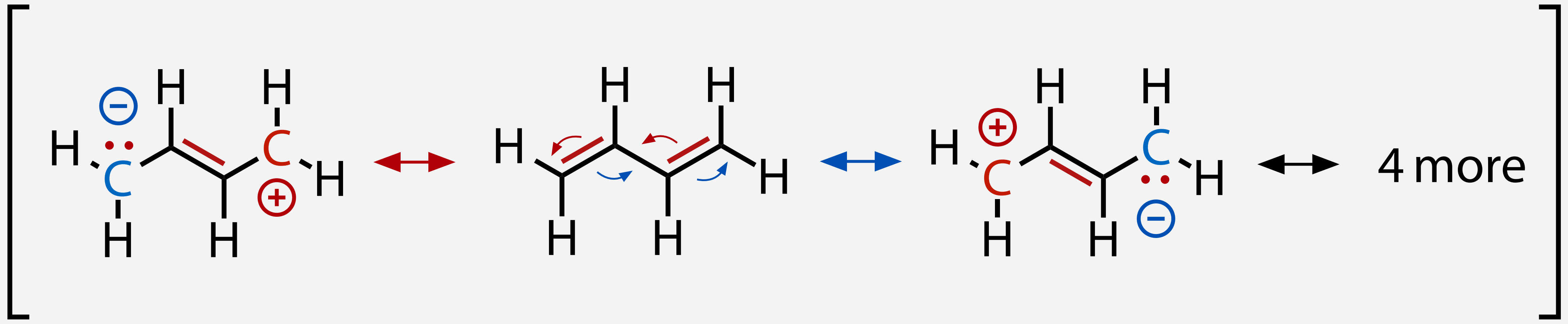
three neutral resonance structures

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

Using Resonance Structures to Compare Delocalization

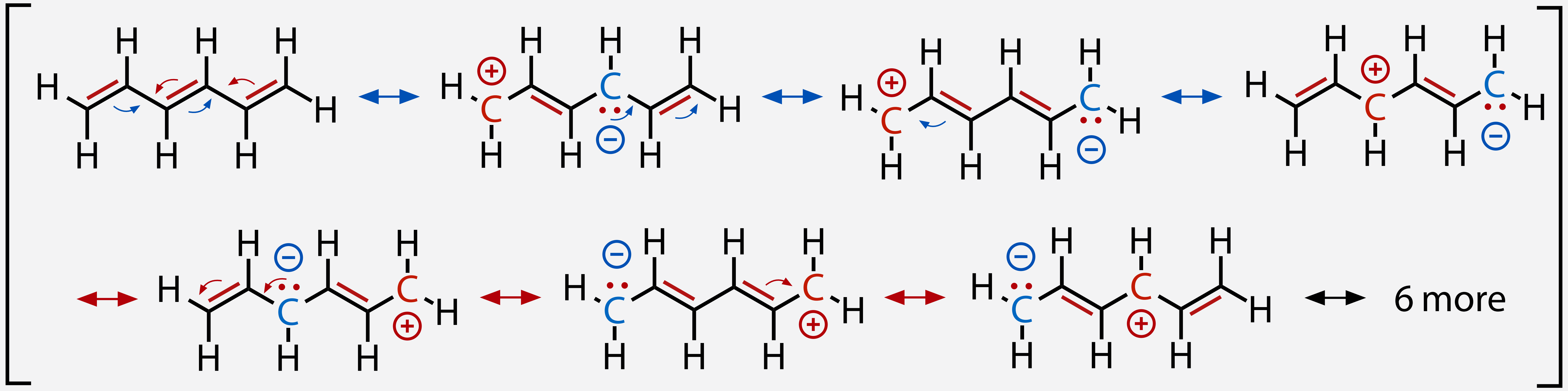
- **degree of delocalization can be estimated from total number of resonance structures**

1,3-butadiene



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

1,3,5-hexatriene



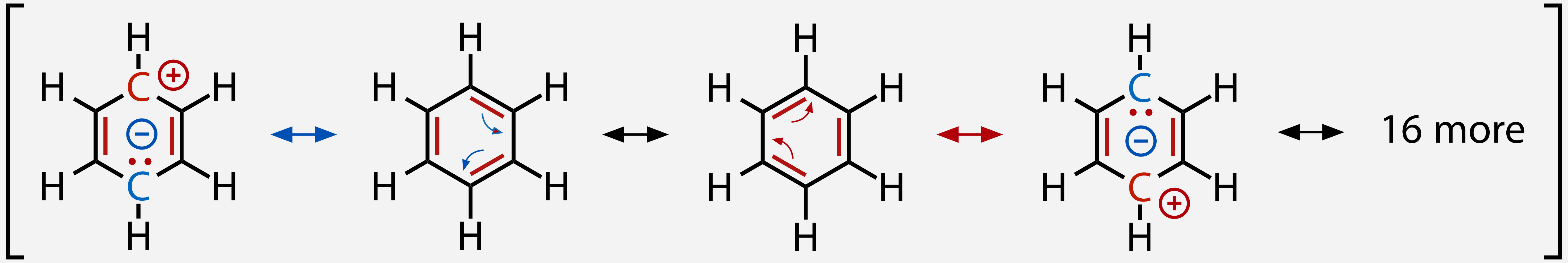
one neutral (major), twelve zwitterionic (minor) resonance structures

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

Using Resonance Structures to Compare Delocalization

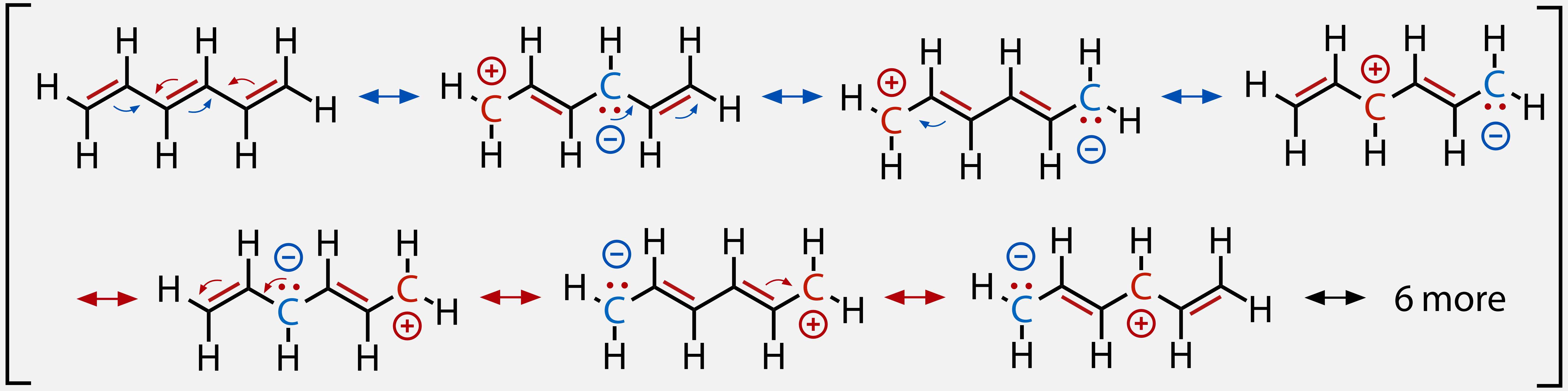
- **degree of delocalization can be estimated from total number of resonance structures**

benzene



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

1,3,5-hexatriene



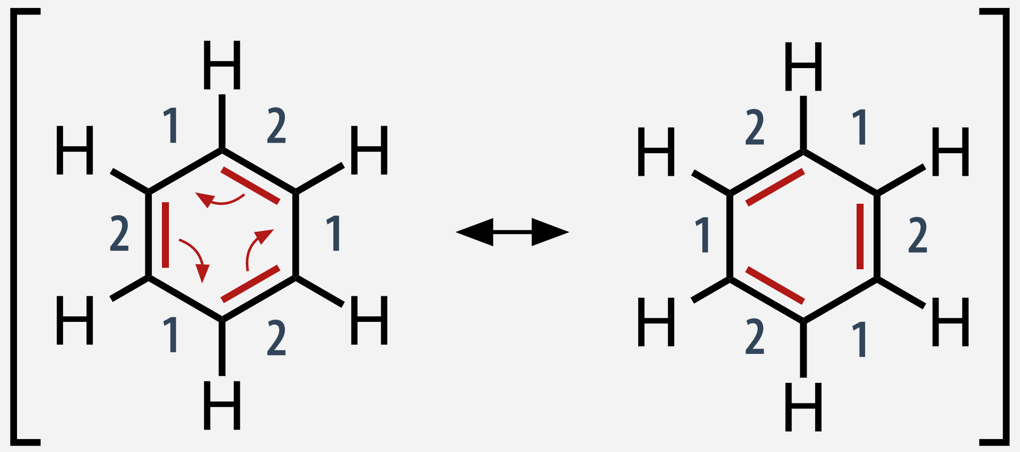
one neutral (major), twelve zwitterionic (minor) resonance structures

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

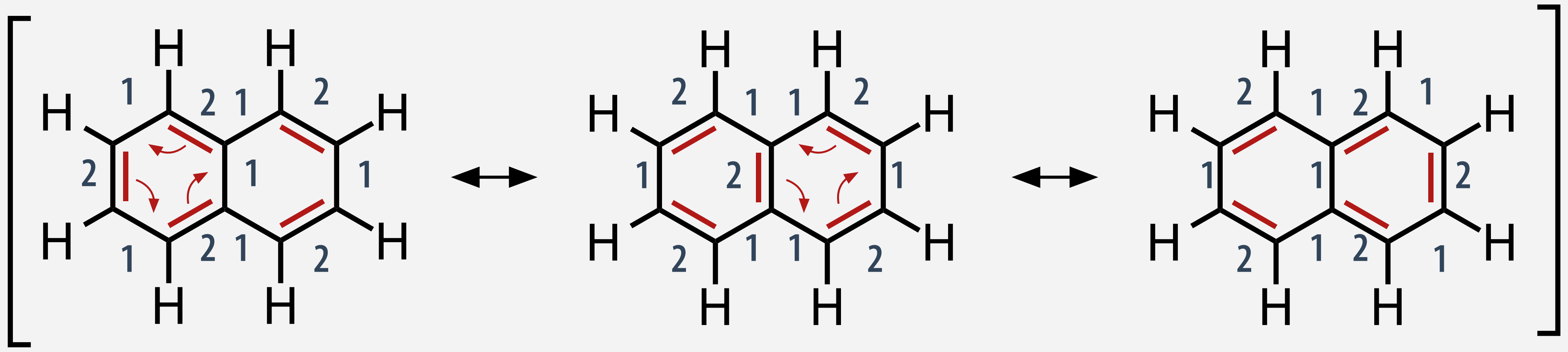
Resonance Structures as an Estimation for Bond Orders

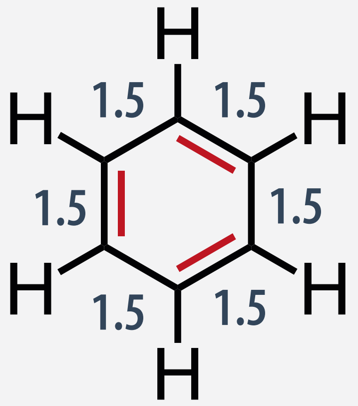
- **ensemble of relevant resonance structures can be used as an approximation for bond orders**

benzene

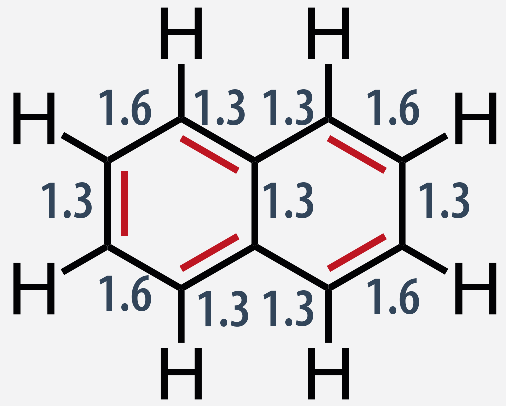


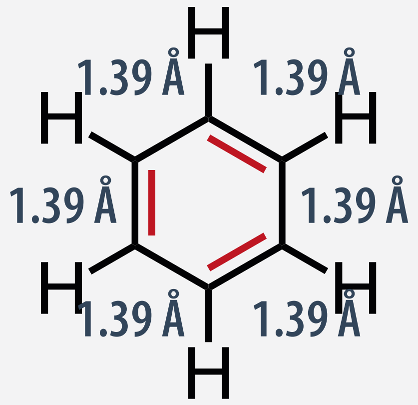
naphthalene



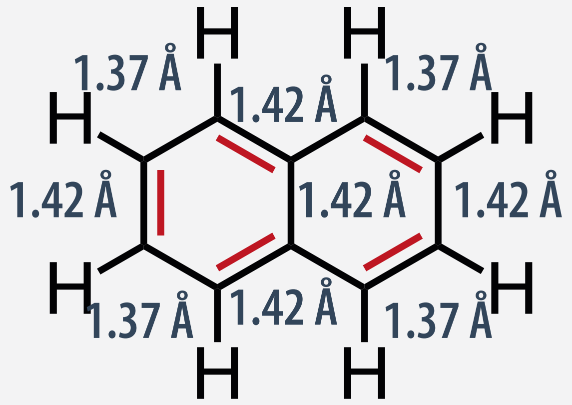


estimated bond orders





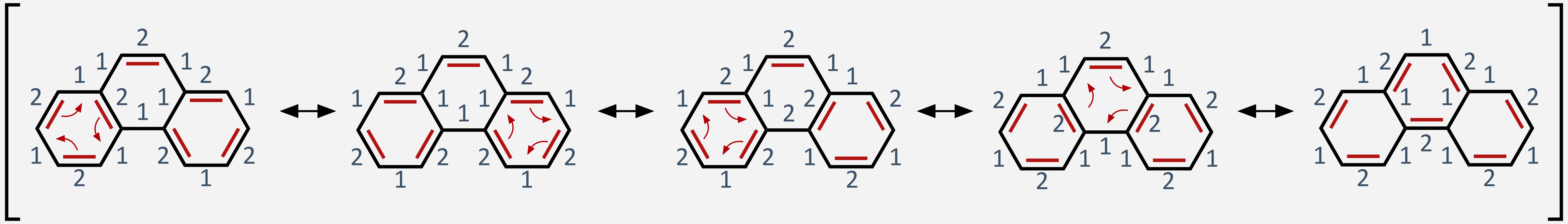
experimental bond lengths

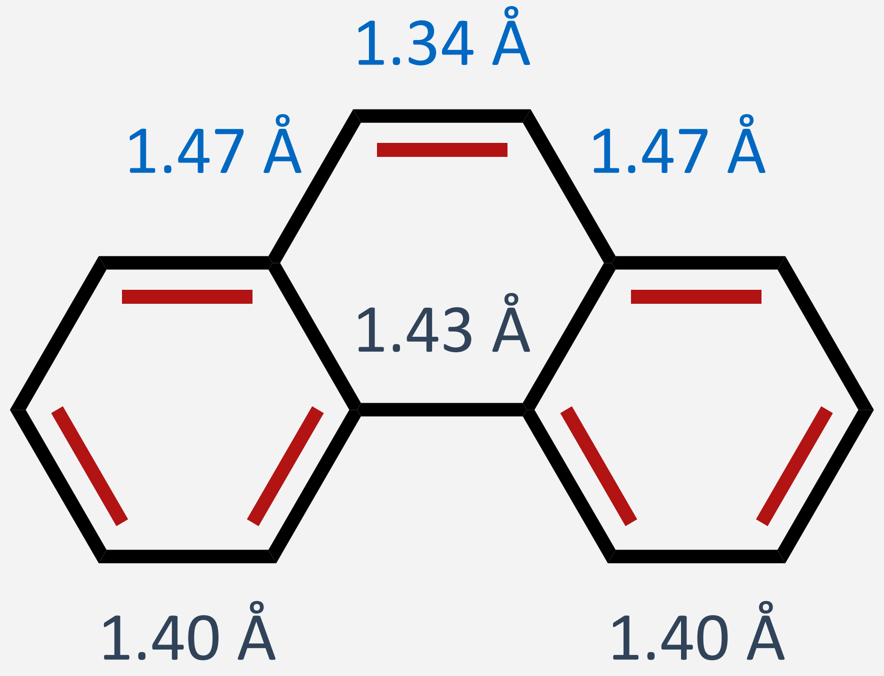


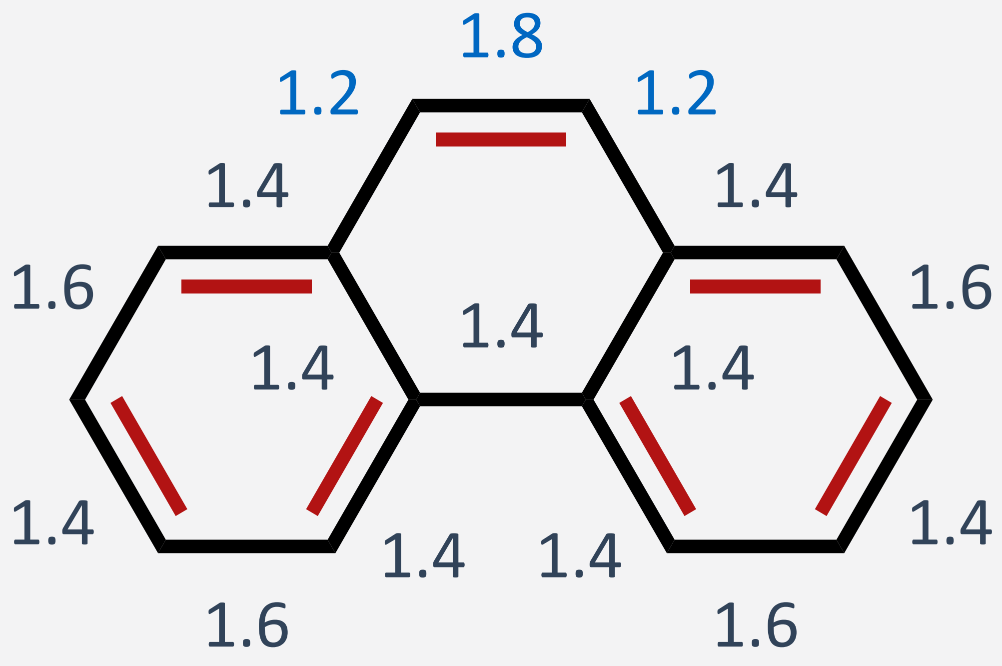
- **determine all relevant resonance structures and individual bond orders in each structure**
- **bond order of a given bond can be estimated from its average over all resonance structures**

Resonance Structures as an Estimation for Bond Orders

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





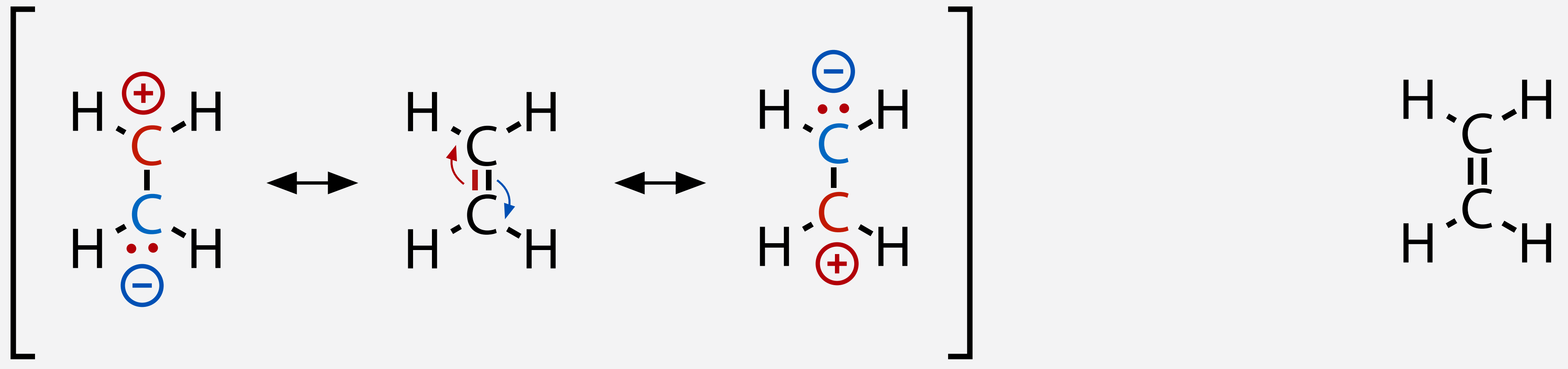


- **determine all relevant resonance structures and individual bond orders in each structure**
- **bond order of a given bond can be estimated from its average over all resonance structures**

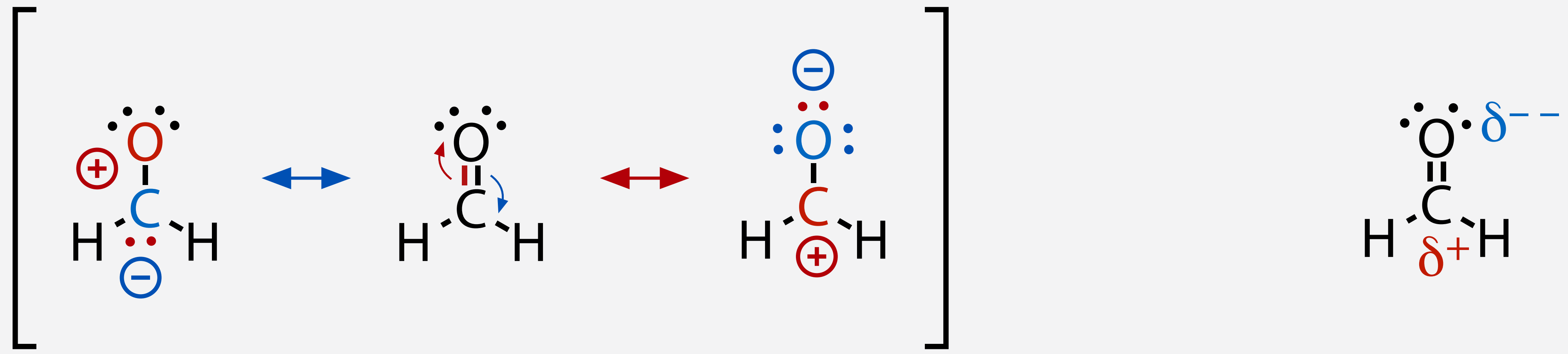
Resonance Structures Involving Electron-Withdrawing Groups

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

ethene


minor major minor

formaldehyde

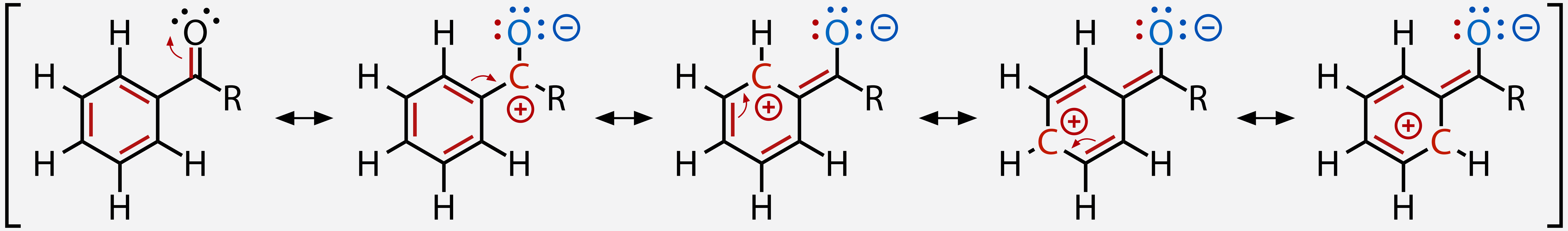


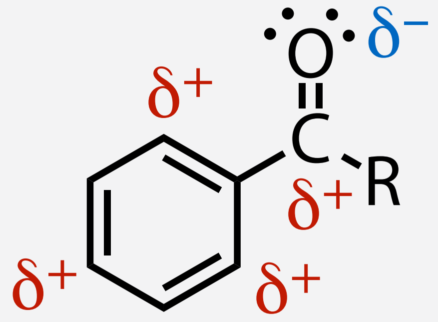
negligible major major

- **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"**

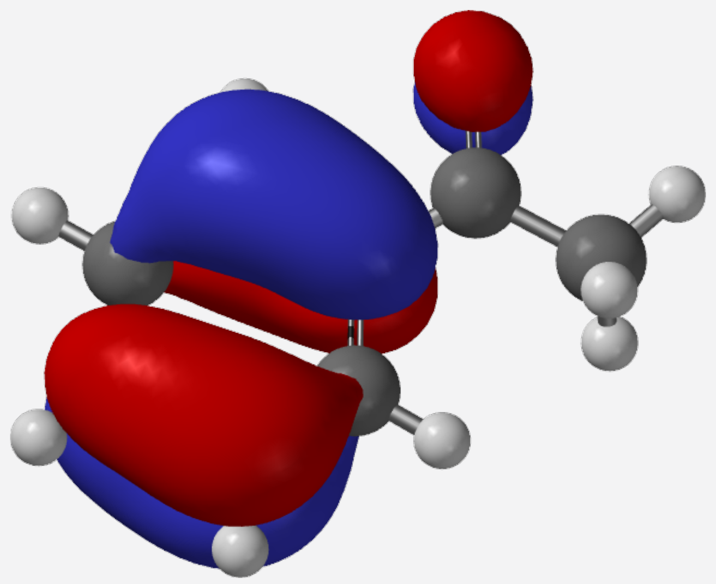
Resonance Structures Involving Electron-Withdrawing Groups

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

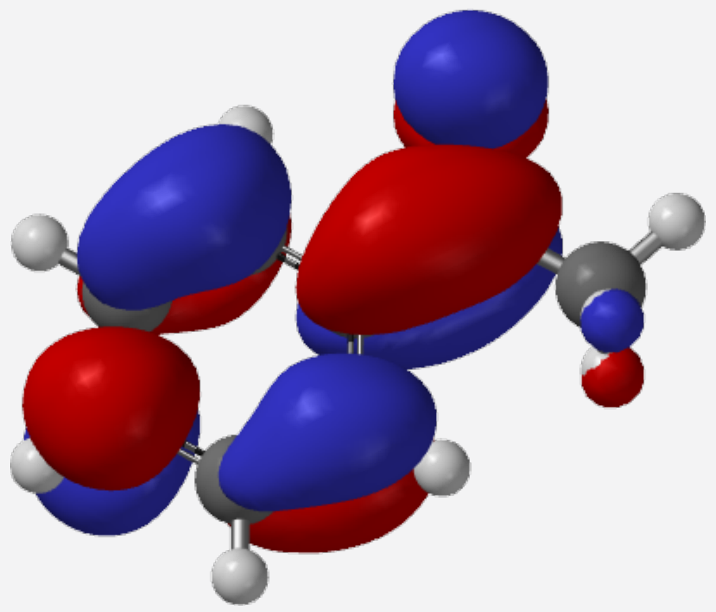




charge distribution



HOMO



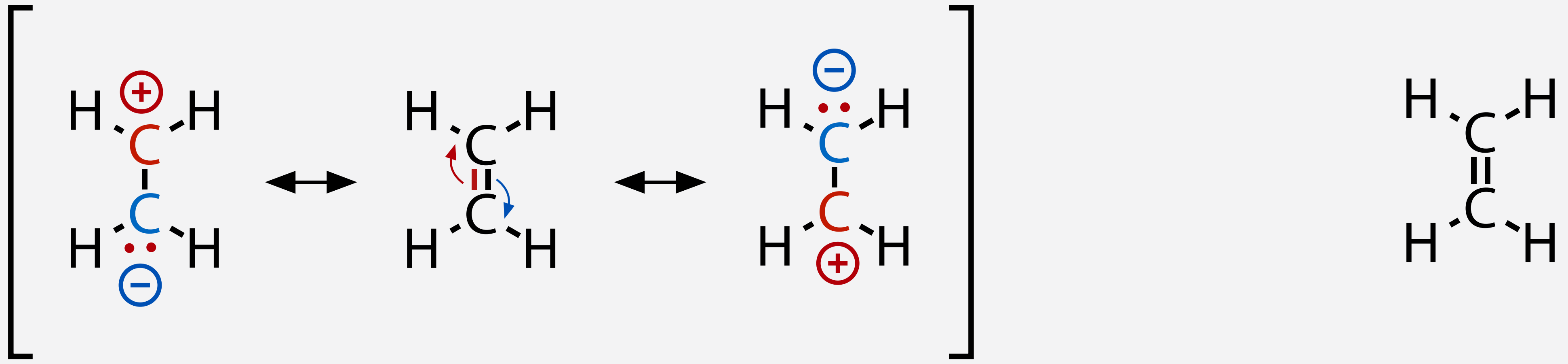
LUMO

- **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**

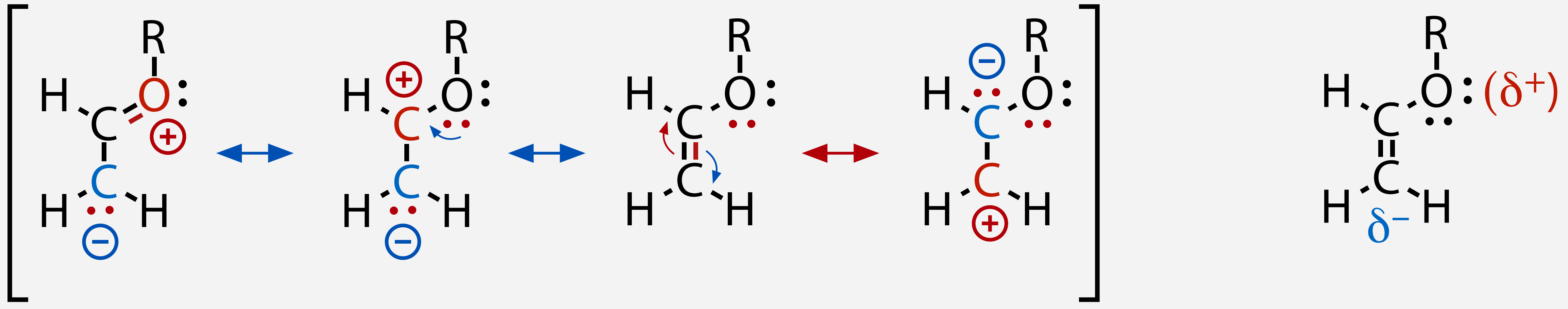
Resonance Structures Involving Electron-Donating Groups

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

ethene



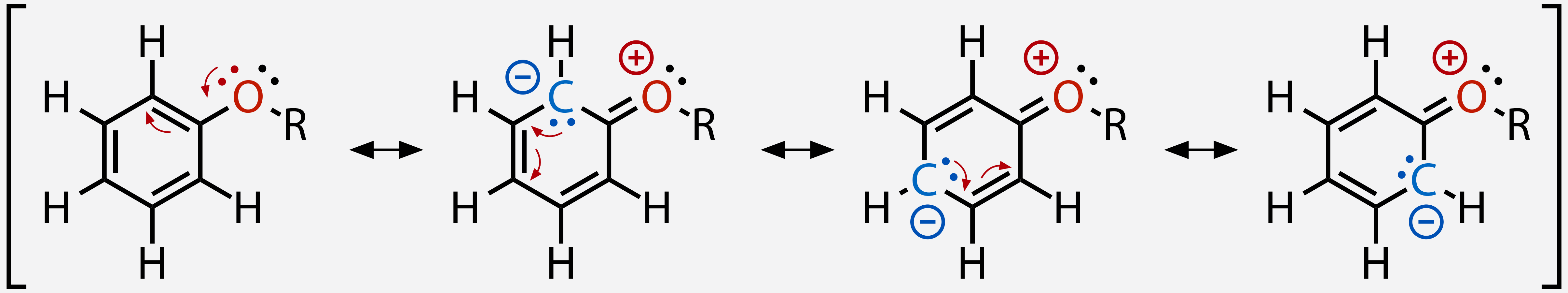
alkoxy ethene

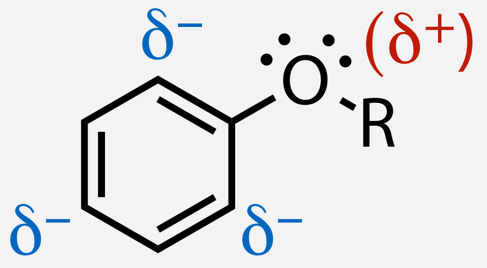


- **positive formal charge on electronegative heteroatoms, but still electron octet!**
- **contrary to all-carbon systems, this results in molecule with strong dipole moment**
- **atoms with free electron pairs are electron-donating “+M substituents”**

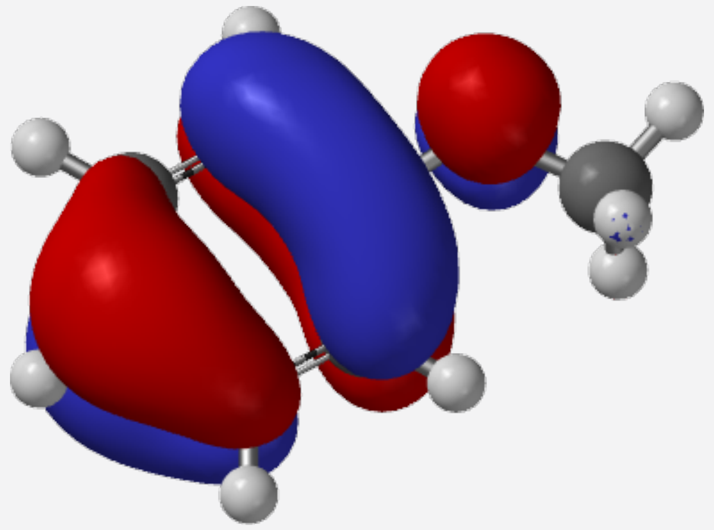
Resonance Structures Involving Electron-Donating Groups

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

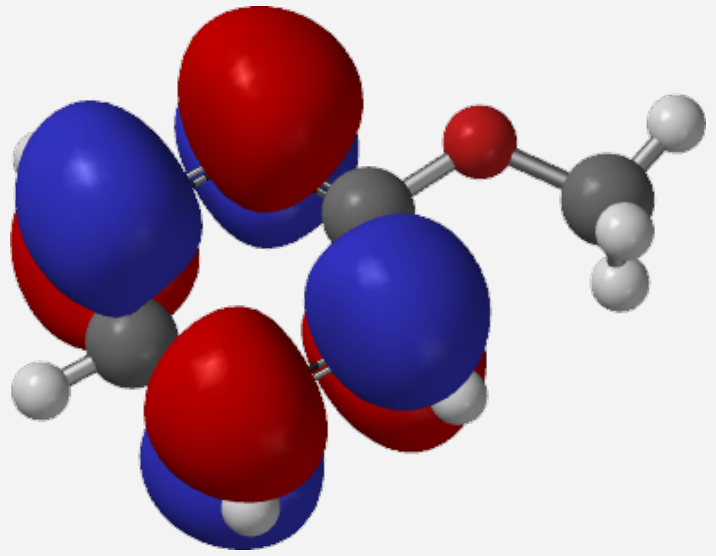




charge distribution



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