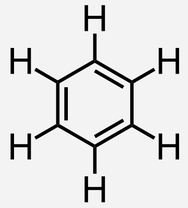
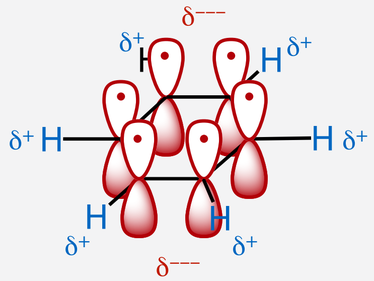
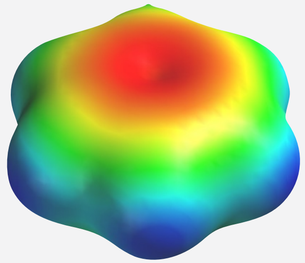
3.1 The Origin of π-Interactions

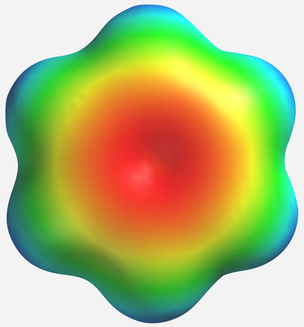
Electron Density Distribution in Molecules with π-Conjugated Systems

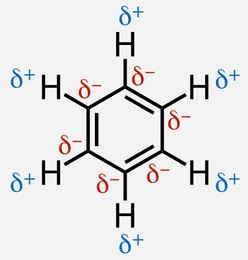


benzene









- due to C–H electronegativity difference, carbons are partially negatively charged
- π-system is polarizable, electron-rich, partially negatively charged
- rim of the molecule is electron-poor, partially positively charged
- benzene has no dipolar moment due to symmetry, but a **quadrupolar moment**

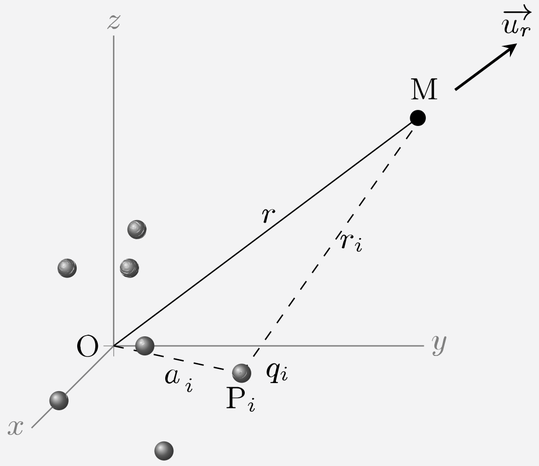
KEY CONCEPT: see Iverson, *Chem. Sci.* **2012**, *3*, 2191.

Quadrupolar Moment

- multipole expansion describing the electrostatic potential of an arbitrary charge distribution:

$$V(M) = \sum_i \frac{q_i}{4\pi\epsilon_0 r}\left[1 + \frac{\overrightarrow{\mathrm{OM}}\cdot\overrightarrow{\mathrm{OP}_i}}{r^2} + \frac{3\left(\overrightarrow{\mathrm{OP}_\mathrm{i}}\cdot\vec{u_r}\right)^2 - \mathrm{OP_i}^2}{2r^2} + o\left(\frac{a_i^2}{r^2}\right)\right]$$

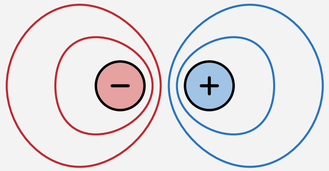
$$V(M) \simeq \frac{\sum_i q_i}{4\pi\epsilon_0\, r} + \frac{\left(\sum_i q_i \overrightarrow{\mathrm{OP}_\mathrm{i}}\right)\cdot\vec{u_r}}{4\pi\epsilon_0\, r^2} + \frac{\mathcal{Q}}{4\pi\epsilon_0\, r^3}$$

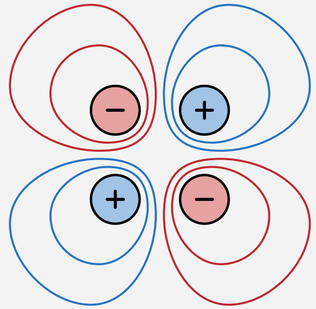


monopole moment
zeroth order

dipole moment
first order

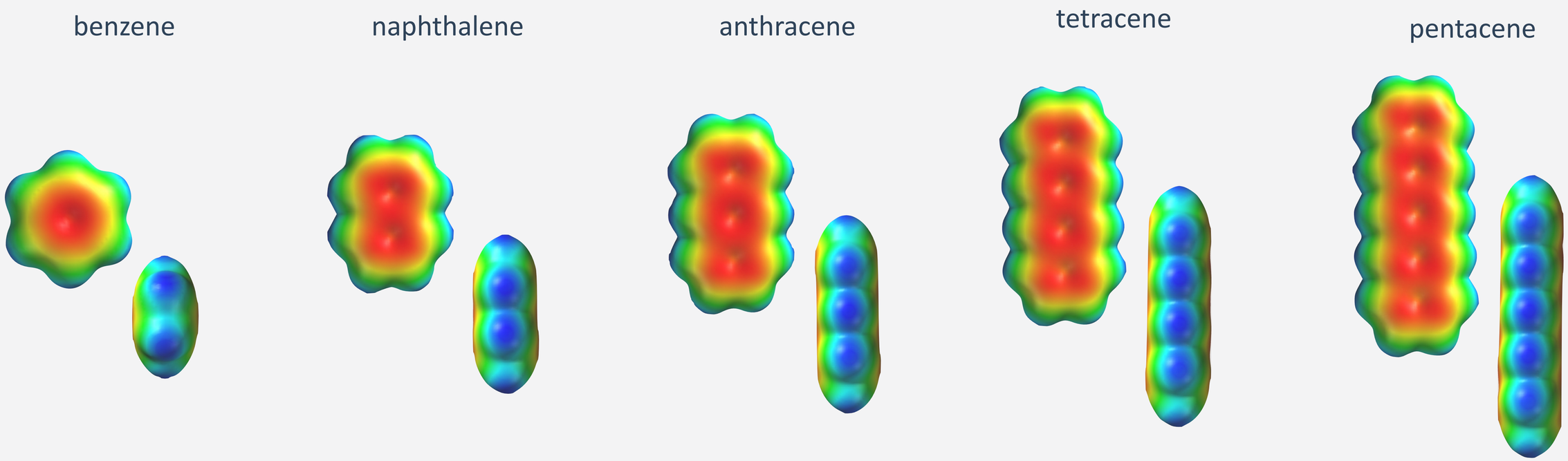
quadrupole moment
second order





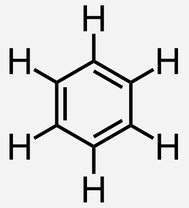
- **quadrupolar moment is second-order term of the electrostatic multipole expansion**

Electron Density Distribution of Increasingly Large π-Conjugated Systems

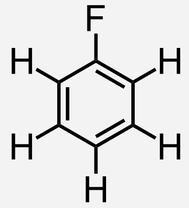


- increasingly large polycyclic π-systems remain **flat** and **rigid** (good for effective dispersive interactions)
- increasingly high-lying HOMO and hence **polarizablity** (important for dispersive interactions)
- increasingly large π **surface area** (crucial for dispersive interactions)
- **quadrupolar moments remain locally the same but become (relatively) less important**

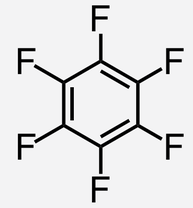
Substituents with Inductive Effects



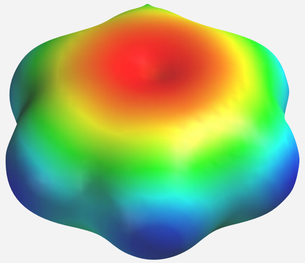
benzene

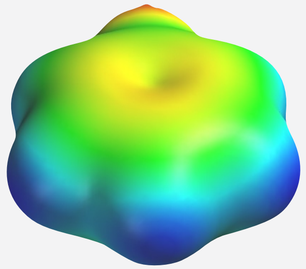


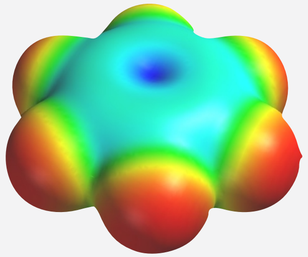
fluorobenzene

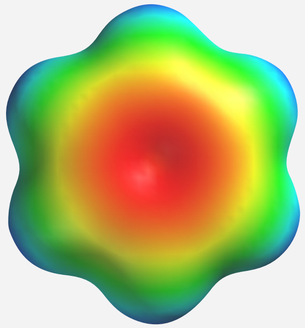


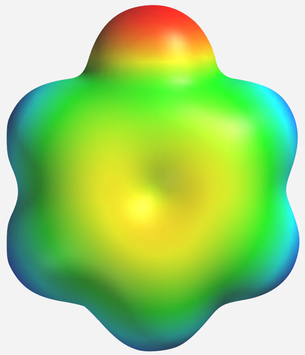
hexafluorobezene

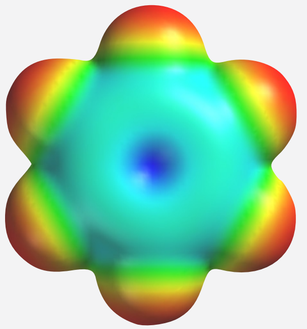






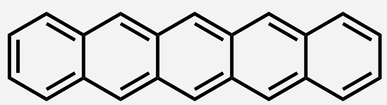




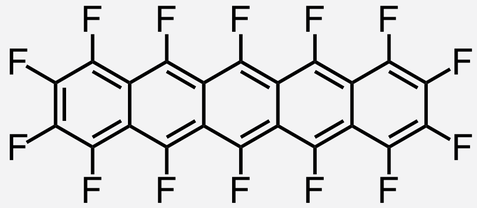


- **inductive effect from electronegative substituents reduces electron density in π-system**

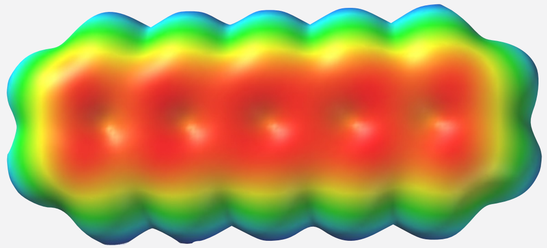
Examples of Electron-rich and Electron Poor π-Conjugated Systems

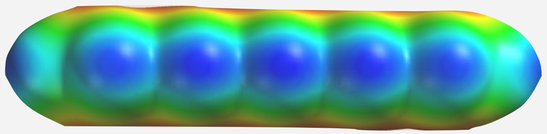


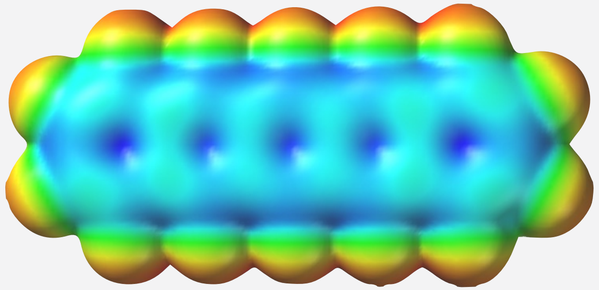
pentacene

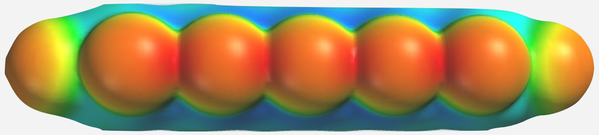


perfluoropentacene





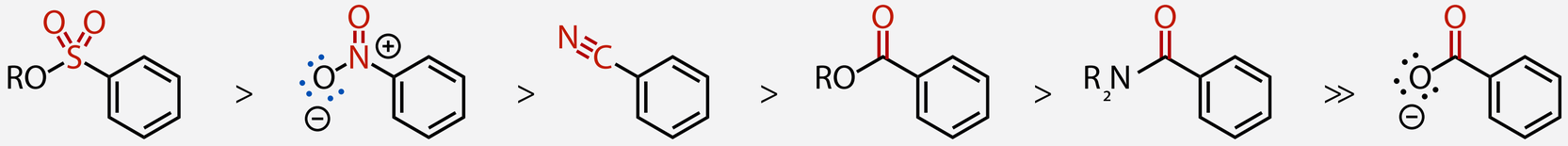


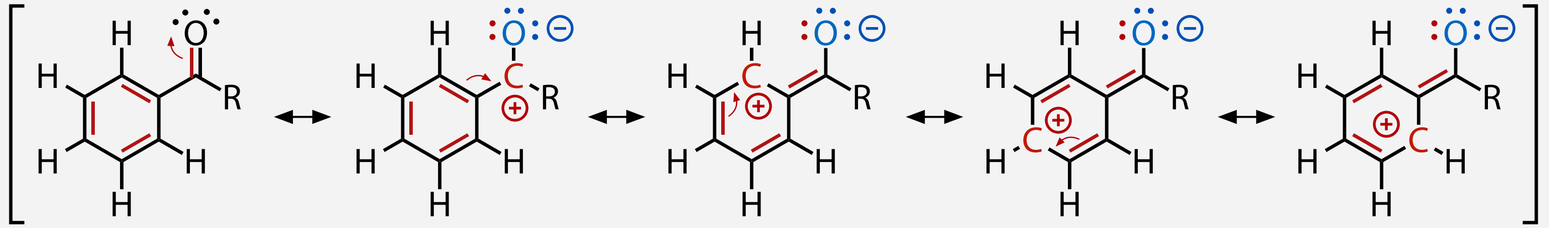


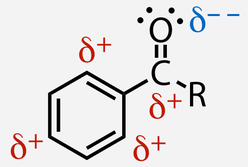
- **perfluorination inverts quadrupolar moment of aromatic systems irrespective of size**

Resonance Structures Involving Electron-Withdrawing Groups

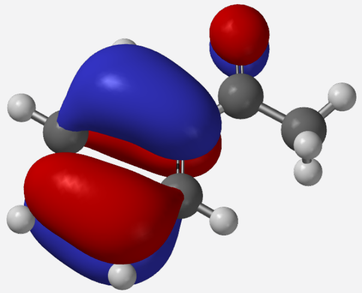
- –M substituents determine electron density and reactivity patterns in π-conjugated systems



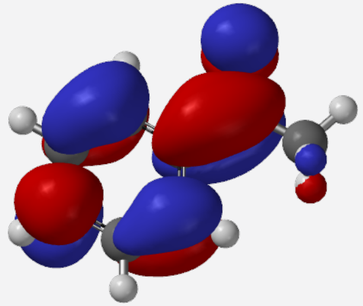




charge distribution



HOMO

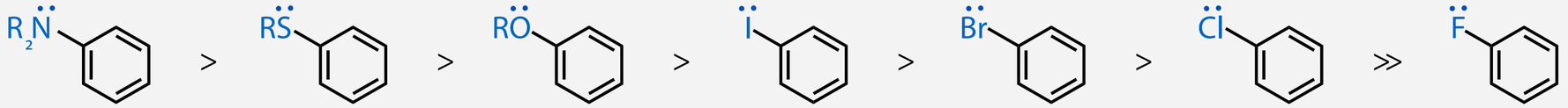


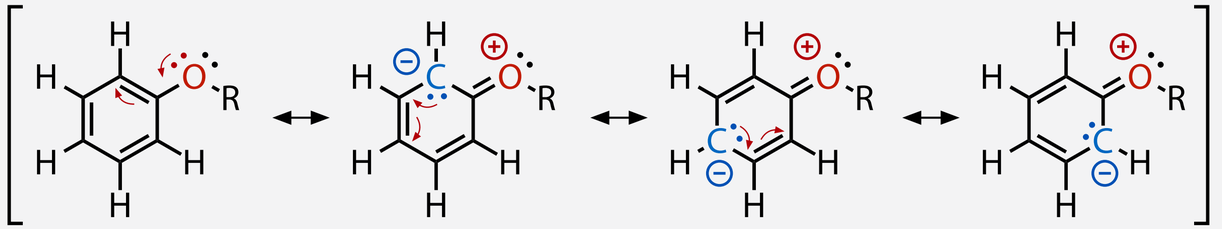
LUMO

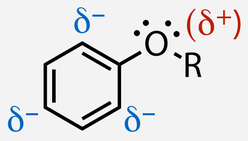
- **overall electron density in the π-system decreased (compared to benzene)**
- **every second carbon in delocalized π system is electron-poor (positive partial charge δ+)**

Resonance Structures Involving Electron-Donating Groups

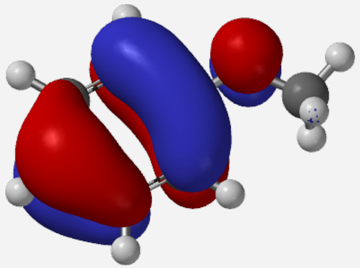
- +M substituents determine electron density and reactivity patterns in π-conjugated systems



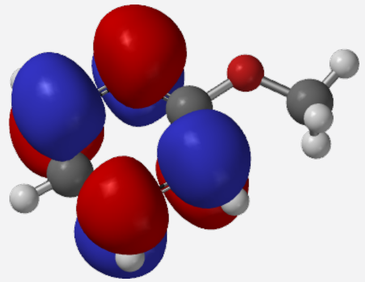




charge distribution



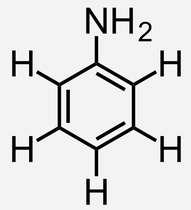
HOMO



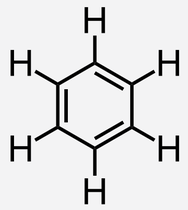
LUMO

- **overall electron density in the π-system increased (compared to benzene)**
- **every other carbon in delocalized π system is electron-rich (negative partial charge δ⁻)**

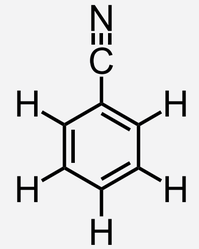
Substituents with Mesomeric Effects



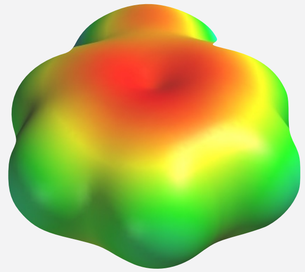
aniline (aminobenzene)

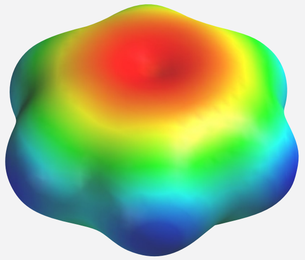


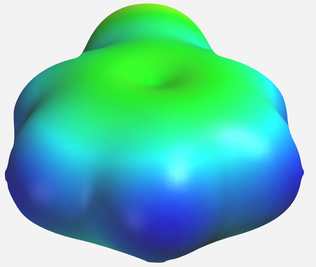
benzene

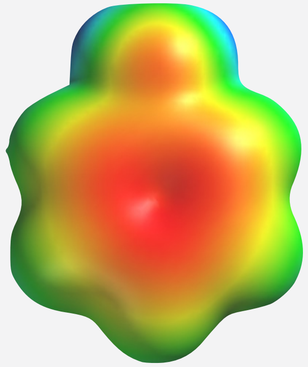


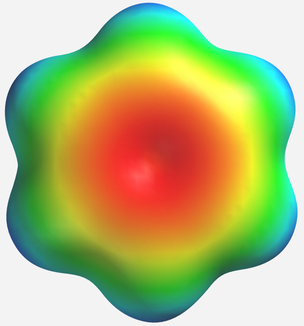
benzonitrile (cyanobenzene)

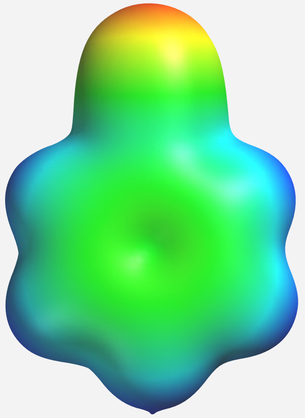






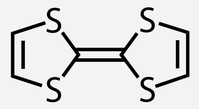




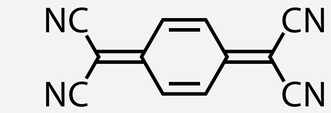


- **mesomeric effects have strong influence on electron density distribution in π-system**

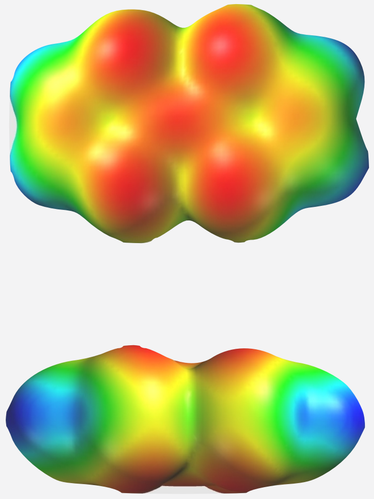
Examples of Electron-rich and Electron Poor π-Conjugated Systems

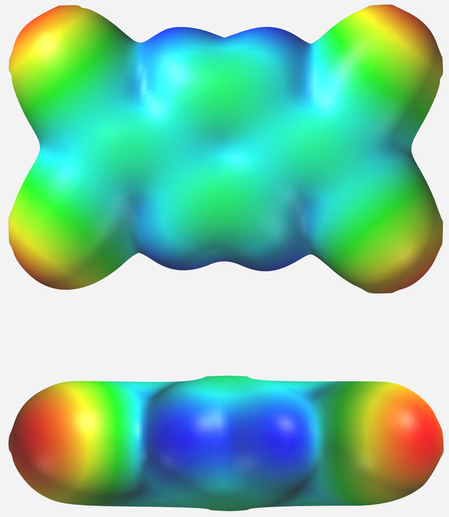


tetrathiafulvalene (TTF)



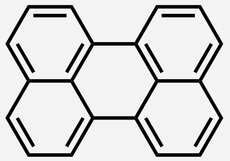
tetracyanoquinodimethane (TCNQ)



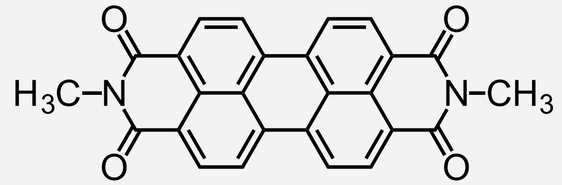


- **heteroatoms with free electron pairs as part of the aromatic system are +M substituents**
- **heteroatom double bonds connected to the π-system are –M substituents**

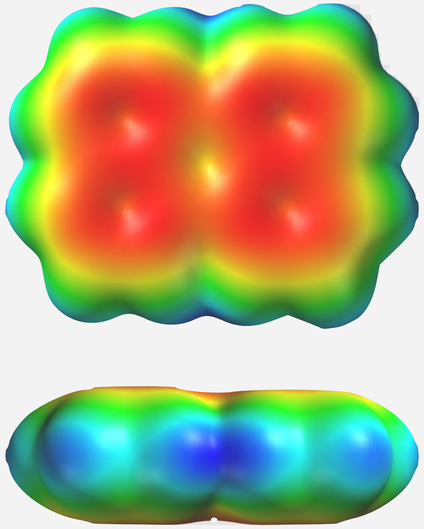
Examples of Electron-rich and Electron Poor π-Conjugated Systems

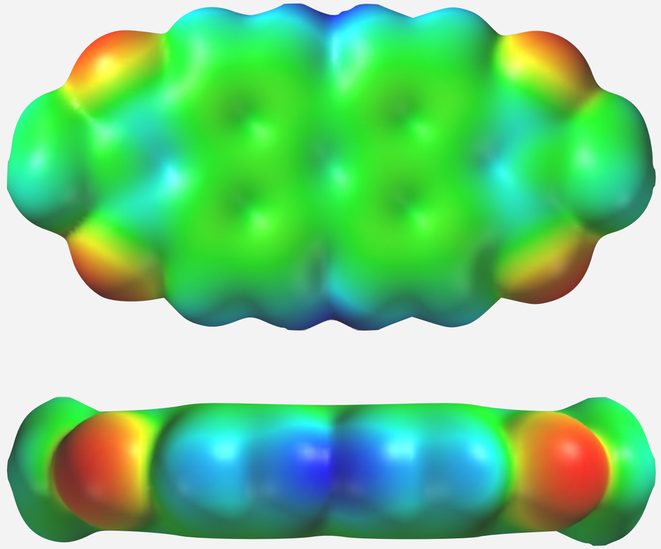


perylene



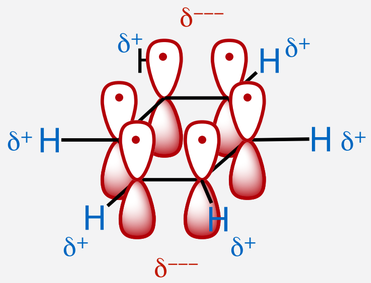
perylene bisimide

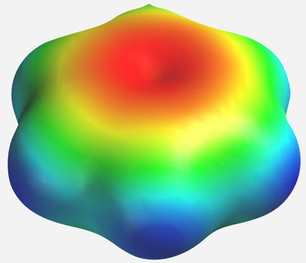


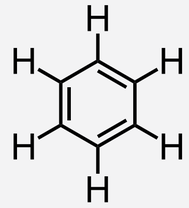


- **–M substituents invert quadrupolar moment of aromatic systems irrespective of size**

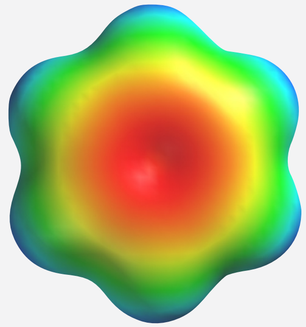
Intermolecular forces between π-conjugated molecules

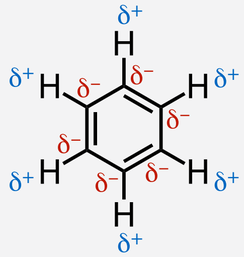






benzene



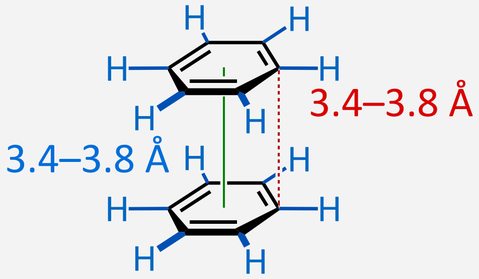


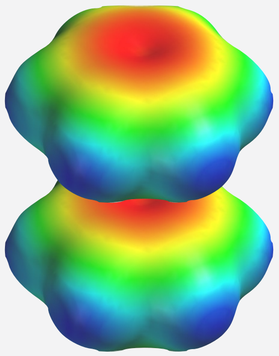
- π-conjugated molecules pack due to three attractive intermolecular forces:
  - Keesom force (electrostatic interaction), the attractive or repulsive interactions between permanent charges, dipoles, and multipoles (quadrupoles in most cases)
  - Debye force (induction interaction), the attractive interactions between a permanent dipole and an induced dipole (only for molecules with polar substituents)
  - London force (dispersive interaction), the attractive interactions between induced dipoles
- π-conjugated molecules pack at Van der Waals distance due to dispersive interactions optimized for quadrupolar moment interactions; MO (exchange) interactions play no role

Packing Patterns for Electron-rich Systems

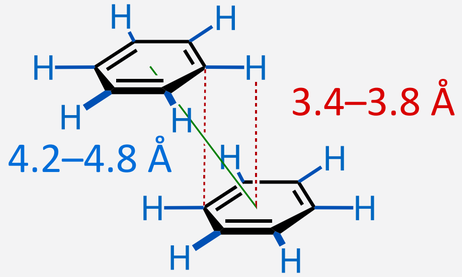
face-to-face π–π stacked

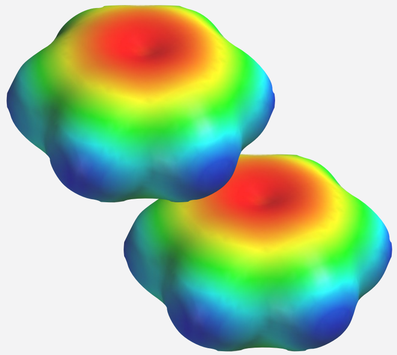
never observed



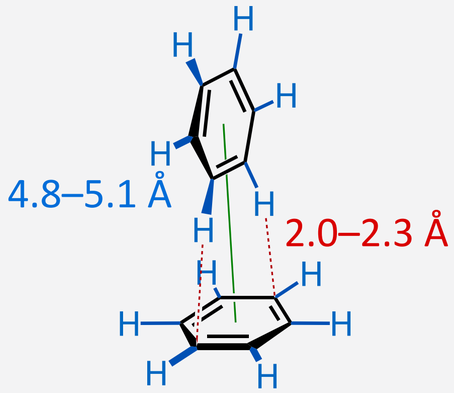


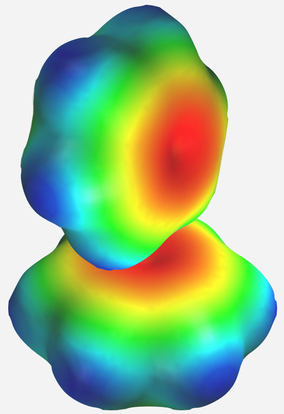
parallel-displaced π–π stacked



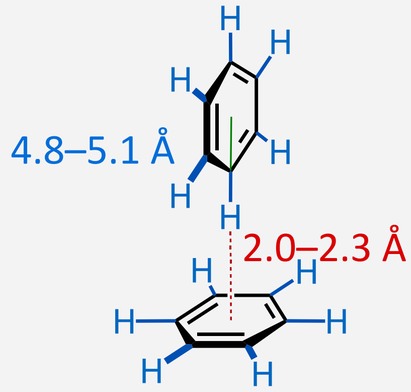


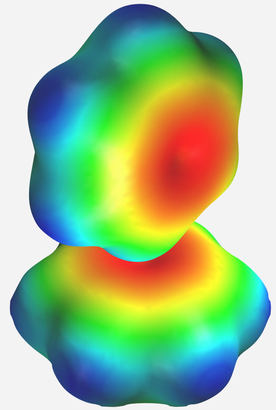
T-shaped edge-to-face





Y-Shaped edge-to-face

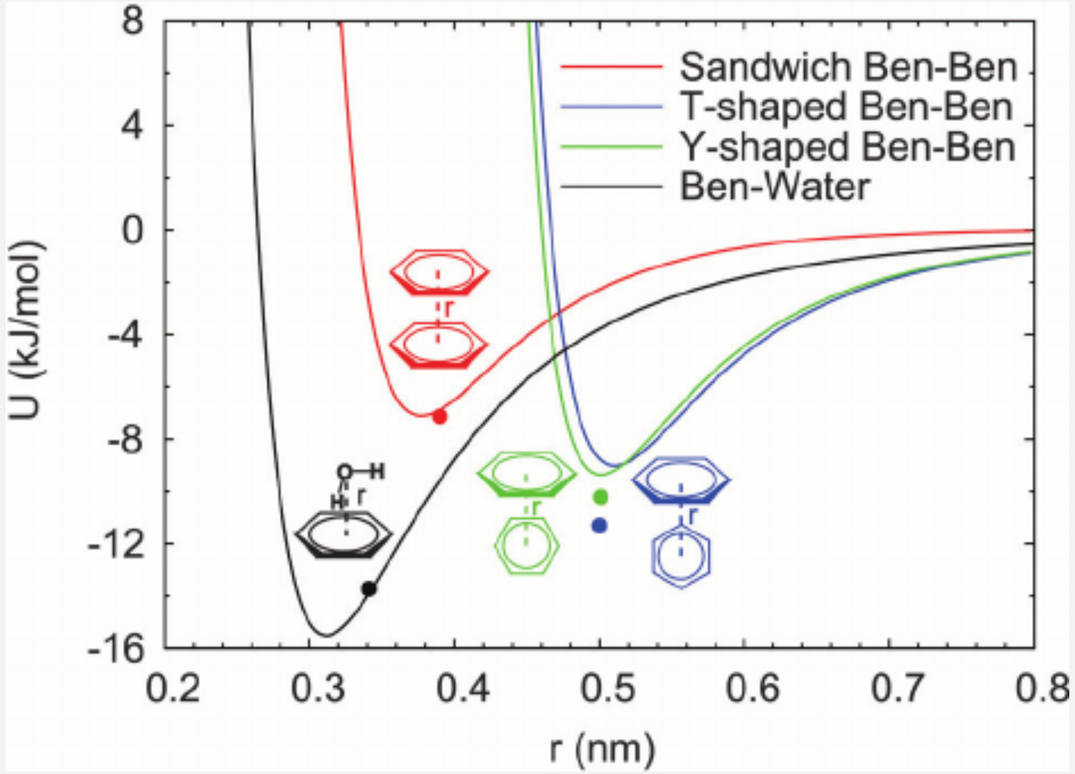




- **π–π interactions are a combination of dispersive interactions with quadrupolar interactions**

Equilibrium π-stacking structure

- molecular crystals forms due to a reduction of potential energy of a multi-molecule system
- relative positions adopted by the molecules in the crystal minimize potential energy



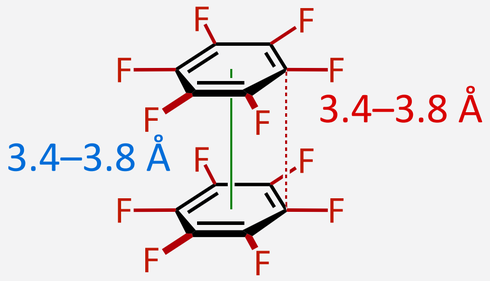
- **π–π interactions are weak (5–50 kJ/mol) and have a short range ($E \propto d^{-6}$)**

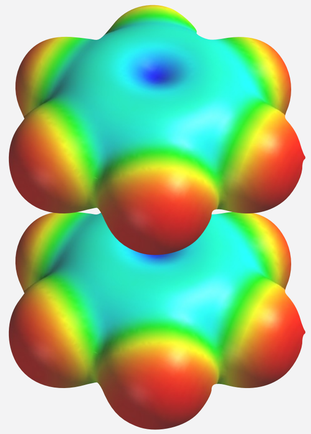
Phys. Chem. Chem. Phys. 2014, *16*, 21957.

Packing Patterns for Electron-poor Systems

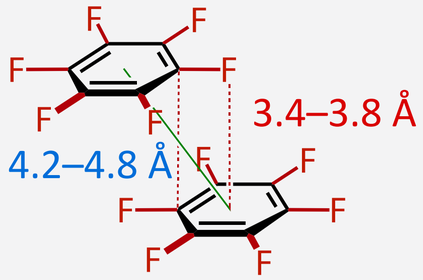
face-to-face
π–π stacked

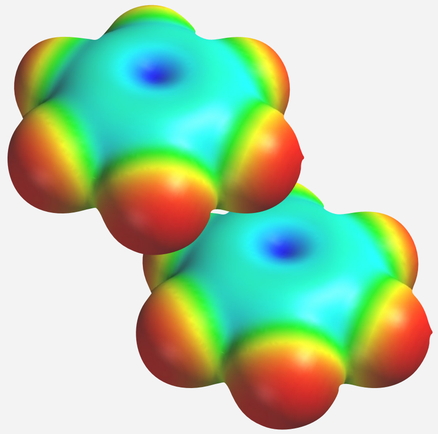
never observed



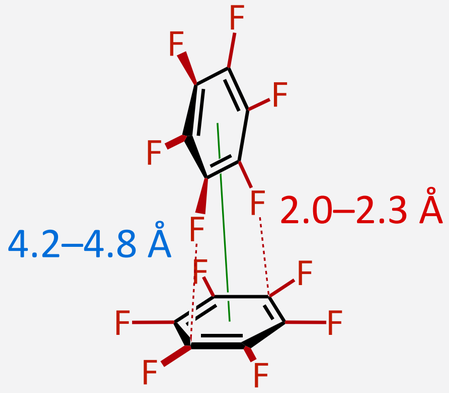


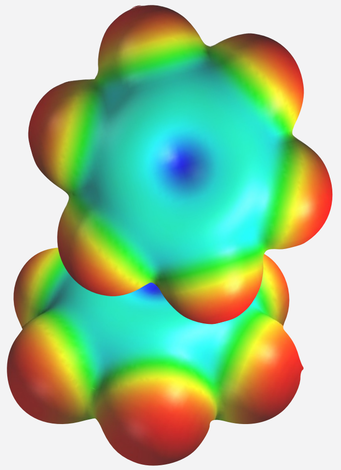
parallel-displaced
π–π stacked



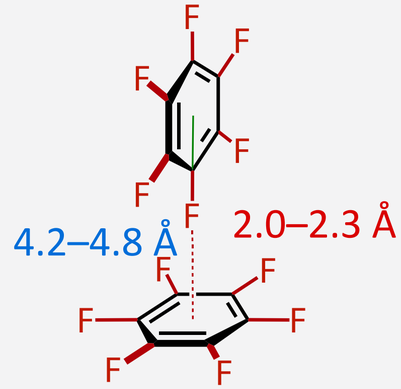


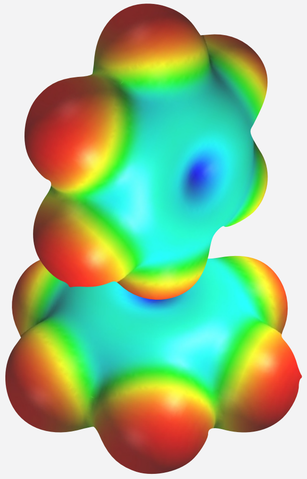
T-shaped
edge-to-face





Y-Shaped
edge-to-face



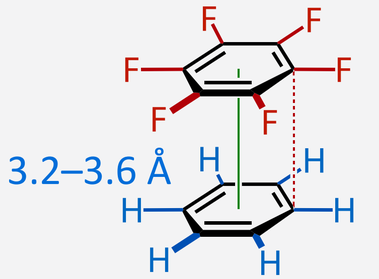


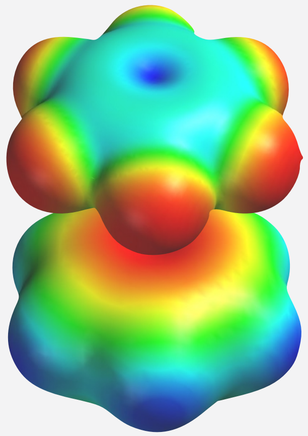
- π–π interactions are a combination of dispersive interactions with quadrupolar interactions

Packing Patterns for Mixed Systems

face-to-face
π–π stacked

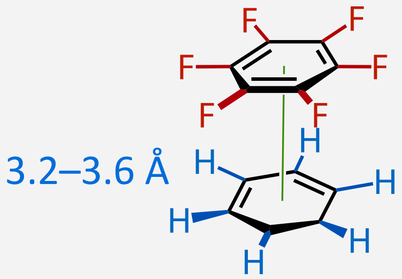
eclipsed

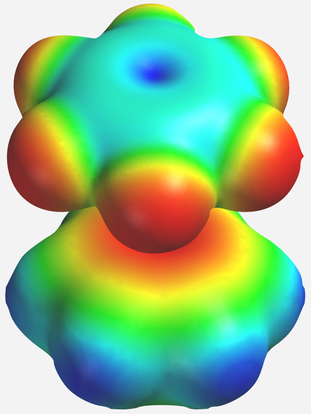




face-to-face
π–π stacked

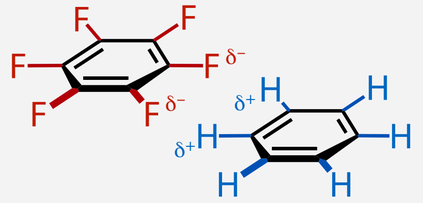
staggered

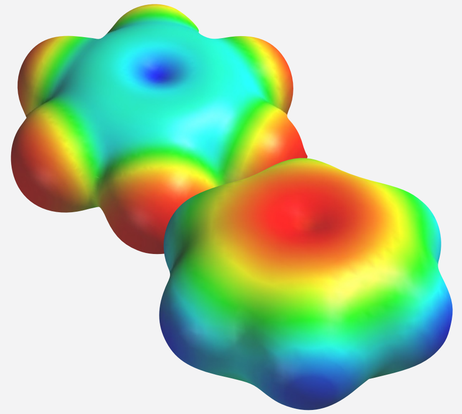




edge-to-edge
dipolar

C–H···F hydrogen bond





- **mixed electron-poor/rich aromatic systems dominated by electrostatic interactions**

Learning Outcome

- **polycyclic π-conjugated systems have quadrupolar moment**
- **rigid system with flat, smooth surface & polarizable π-system for good dispersive interactions**
- **supramolecular packing balances intermolecular forces and minimizes the associated total potential energy**
  - typical motif is parallel-displaced π–π stacking
  - another typical motif is the edge-to-face orientation
  - ideally, periodic packing in the solid state accommodates both motifs