Chemistry II (Organic): Introduction to Stereoelectronics

A Highly Qualitative Organic Chemists Guide to Orbital Interactions and Stereoelectronic Phenomena

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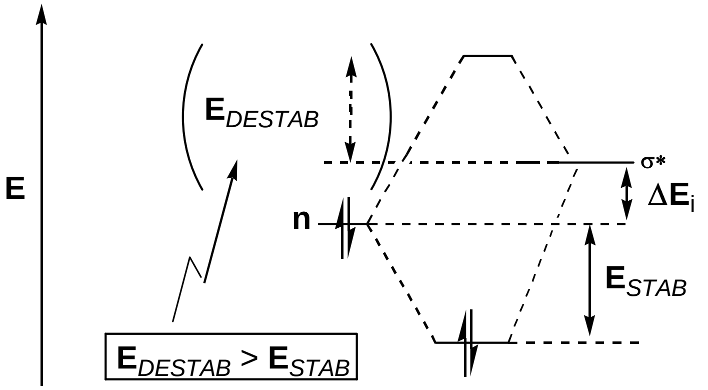
Stereoelectronic effects arise as the result of overlap of molecular orbitals on adjacent atoms. Stabilising (attractive) interactions result from 2 (and 1) electron interactions. Destabilising (repulsive) interactions result from 4 electron interactions:

e.g.



$$\boxed{E_{STAB} \; \alpha \; \frac{S^2}{\Delta E_i}}$$

S^2 = overlap integral

E_{STAB} = stabilisation energy

ΔE_i = interaction energy

For maximum $\mathbf{E}_{STAB}$ (i.e. large 'effect') we need:

- large **OVERLAP INTEGRAL**
- small **INTERACTION ENERGY**, ΔE_I (i.e. difference in energy between orbitals)

The **OVERLAP INTEGRAL** is strongly dependent of two factors:

(1) Relative orientation of interacting orbitals:

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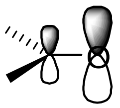
	syn-periplanar:	OK
	anything else:	BAD

(2) The co-efficients (i.e. size) of interacting orbitals: bigger co-efficient FAVOURABLE

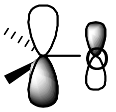
These can be estimated from electronegativity data: e.g. (π 'polarisation')

NB. the 'intuitive' polarisation is that of the π-bonding orbital...the anti-bonding π* orbital shows the 'opposite' polarisation. (This holds true for σ and σ* too).



π

cf.



π*

Assessment of the **INTERACTION ENERGY**, ΔE_I is difficult but the following are guidelines:

Within the same molecule 'frontier' bonding orbitals will be of LOWER energy than 'frontier' anti-bonding orbitals…and this usually holds between molecules too (see over).

For C-X σ bonds: X = Electron withdrawing (electronegative) → LOWERS the energy of both σ and σ^*
X = Electron releasing (electropositive) → RAISES the energy of both σ and σ^*

Lewis Acid interactions with e.g. a carbonyl group → LOWERS the energy of both π and π^*

As a result of the above considerations the following series have been constructed:

MOST EFFECTIVE **DONOR** ORBITALS: $\mathbf{n}_{C^{\ominus}} > \mathbf{n}_N > \mathbf{n}_S > \mathbf{n}_O > \sigma_{C\text{-}S} > \underbrace{\sigma_{C\text{-}H} \geqslant \sigma_{C\text{-}C}}_{\text{DISPUTED}} > \sigma_{C\text{-}O} > \sigma_{C\text{-}F}$

MOST EFFECTIVE **ACCEPTOR** ORBITALS: $\mathbf{p}_{vac} > \sigma^*_{C\text{-}Cl} > \sigma^*_{C\text{-}S} > \sigma^*_{C\text{-}F} > \sigma^*_{C\text{-}O} > \sigma^*_{C\text{-}C} \simeq \sigma^*_{C\text{-}H}$

Consequently $\mathbf{n} \rightarrow \sigma^*$ ('anomeric') interactions are usually stronger than $\sigma \rightarrow \sigma^*$ ('Cieplak') ones.

For an excellent paper on the fundamentals of stereoelectronic effects and acceptor ability of σ-bonds in particular see: I.V. Alabugin and T.A. Zeidan *J. Am. Chem. Soc.* **2002**, *124*, 3175.

The important interactions are:

$\mathbf{n} \rightarrow \sigma^*$ 'ANOMERIC'
$\sigma \rightarrow \sigma^*$ 'CIEPLAK'
$\pi \rightarrow \sigma^*$ 'NEGATIVE HYPERCONJUGATION'

$$\left.\begin{array}{l} cf.\ \sigma \rightarrow \pi^* \\ \sigma \rightarrow \mathbf{p}_{vac} \end{array}\right] \text{'HYPERCONJUGATION'}$$

$$\left.\begin{array}{l} \mathbf{n} \rightarrow \pi^* \\ \mathbf{n} \rightarrow \mathbf{p}_{vac} \\ \pi \rightarrow \pi^* \\ \pi \rightarrow \mathbf{p}_{vac} \end{array}\right] \text{'RESONANCE'}$$

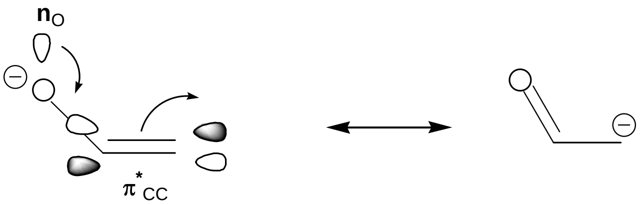
KIRBY'S THEORY: "There is a stereoelectronic preference for conformations in which the best donor lone pair or bond is ***anti-peri planar*** to the best acceptor bond or orbital"

DESLONGCHAMPS' THEORY: "TWO STEREOELECTRONIC INTERACTIONS ARE BETTER THAN ONE!"

…Hence the stability of dispiroketal protecting groups (see 'anomeric effect' handout) as the result multiple anomeric effects. BUT beware, a molecule can only adopt one conformation at any one instant in time and so multiple stereoelectronic effects are only additive in a single conformation. If two competing stereoelectronic interactions require two different conformations then, all other factors being equal, the molecule will adopt the conformation which allows the more stabilising interaction to occur.

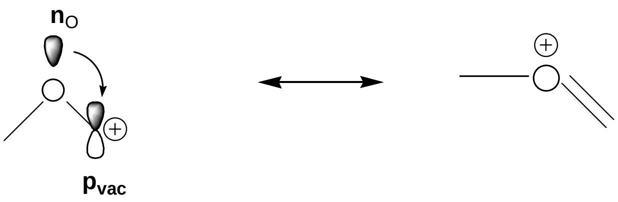
Important Orbital Interactions in Organic Chemistry:

n to π*



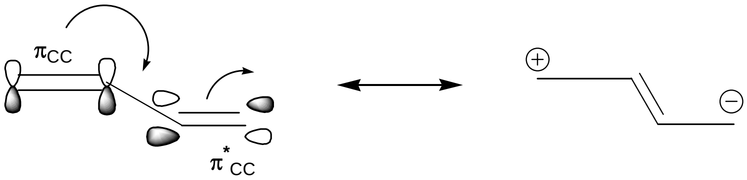
Resonance
e.g.
- enolate anion
- allyl anion

n to p_{vac}



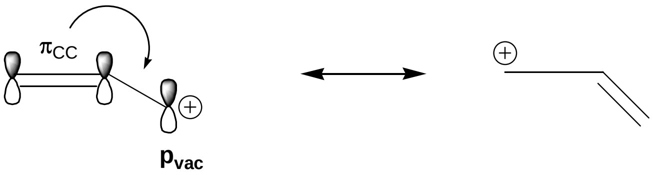
Resonance
e.g.
- oxonium ions

π to π*



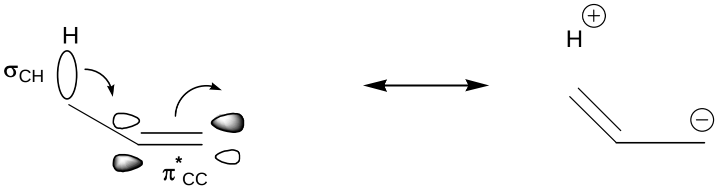
Resonance
e.g.
- conjugated alkenes
- α,β-unsat carbonyls

π to p_{vac}



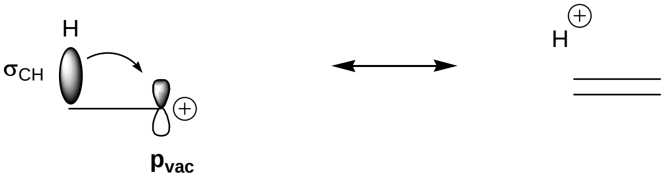
Resonance
e.g.
- allylic cations
- benzylic cations

σ to π*



Hyperconjugation
e.g.
- stabilisation of more substituted double bonds

σ to p_{vac}



Hyperconjugation
e.g.
- stabilisation of more substituted carbocations
- silicon β-effect

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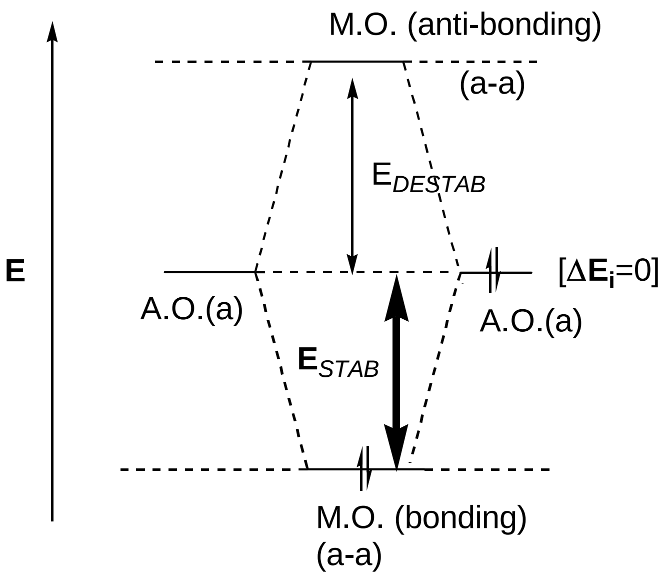
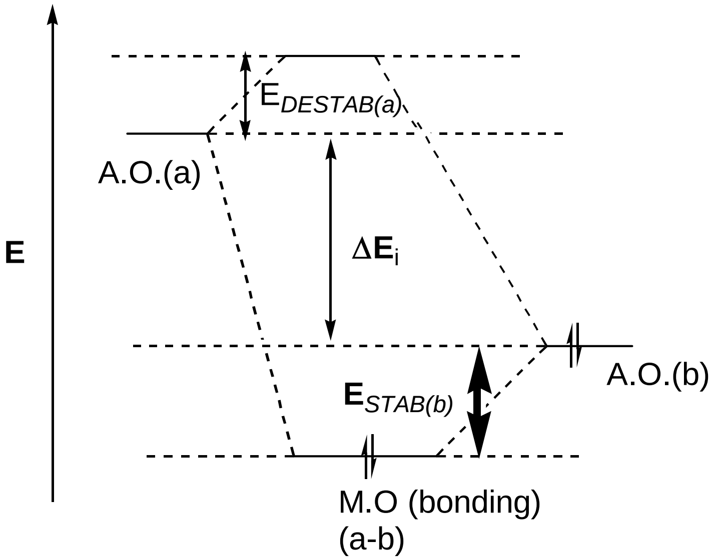
Orbital Interaction Diagram for an “a-a” System:



- ## Orbital Interaction Diagram for an “a-b” System:



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