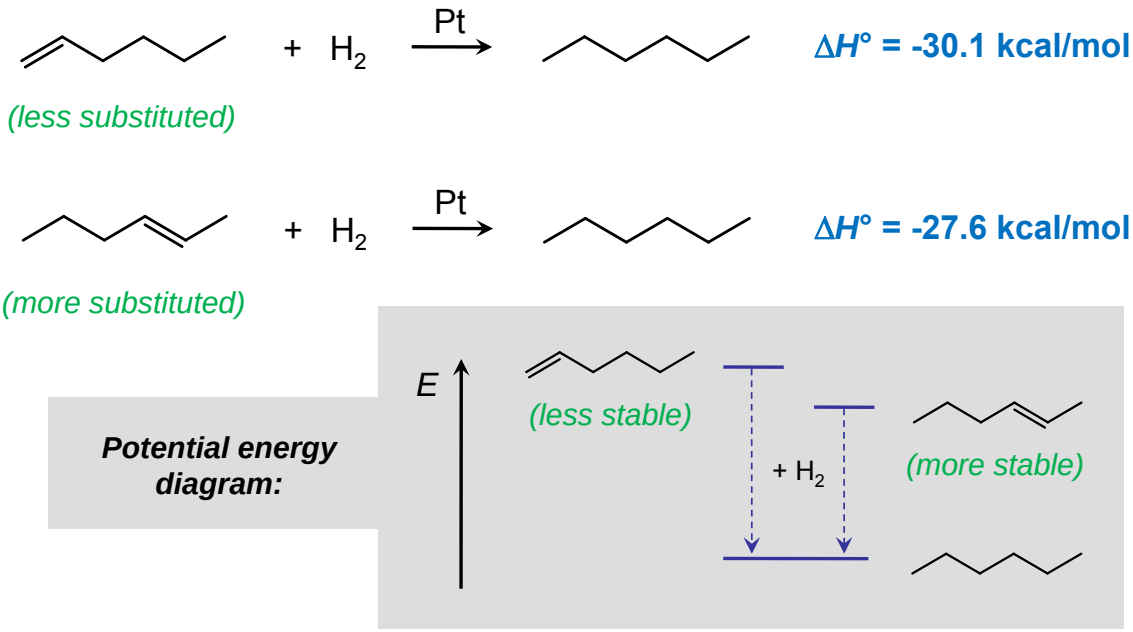
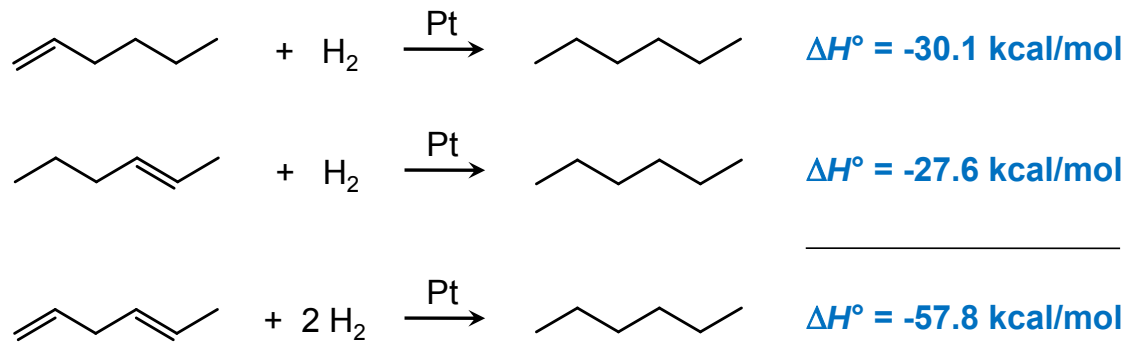
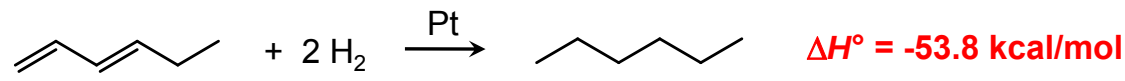
Relative Stabilities of Alkenes Are Illustrated by Heat of Hydrogenation



Adjacent ("Conjugated") Double Bonds Are More Stable Than Isolated Ones

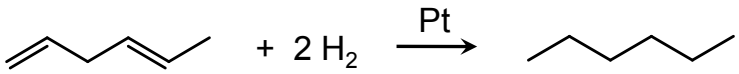


Makes great sense: Energy from two hydrogenations is sum of single hydrogenations.

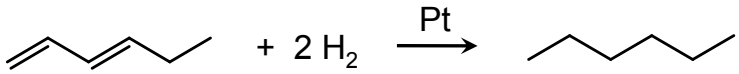


Makes less sense. Energy from hydrogenation of two adjacent alkenes is **4 kcal/mol less** than expected.

Adjacent ("Conjugated") Double Bonds Are More Stable Than Isolated Ones

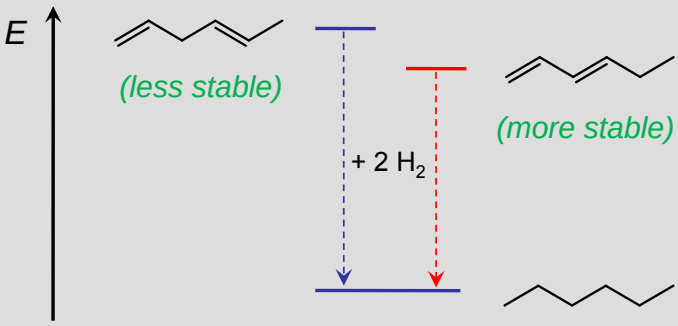


$\Delta H° = -57.8$ kcal/mol



$\Delta H° = -53.8$ kcal/mol

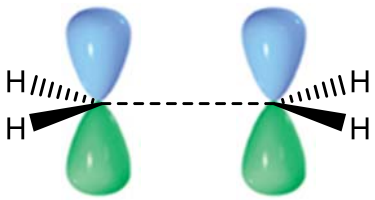
Potential energy diagram:



Hypothesis:

Extra stability ("resonance energy") is due to molecular orbital interactions.

Review: Constructing Molecular Orbitals by Mixing Atomic Orbitals



How do we describe a π bond in terms of molecular orbitals?

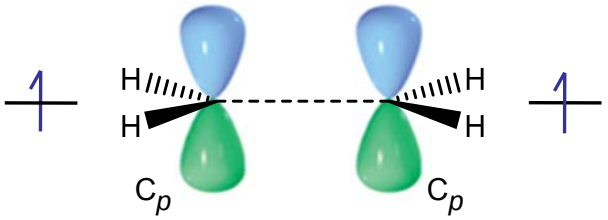
Make from atomic *p* orbitals.

Guidelines for orbital mixing:

Molecular orbitals look like combinations of starting orbitals, with some distortions.

You end with the same number of orbitals you started with.

Review: Constructing Molecular Orbitals by Mixing Atomic Orbitals



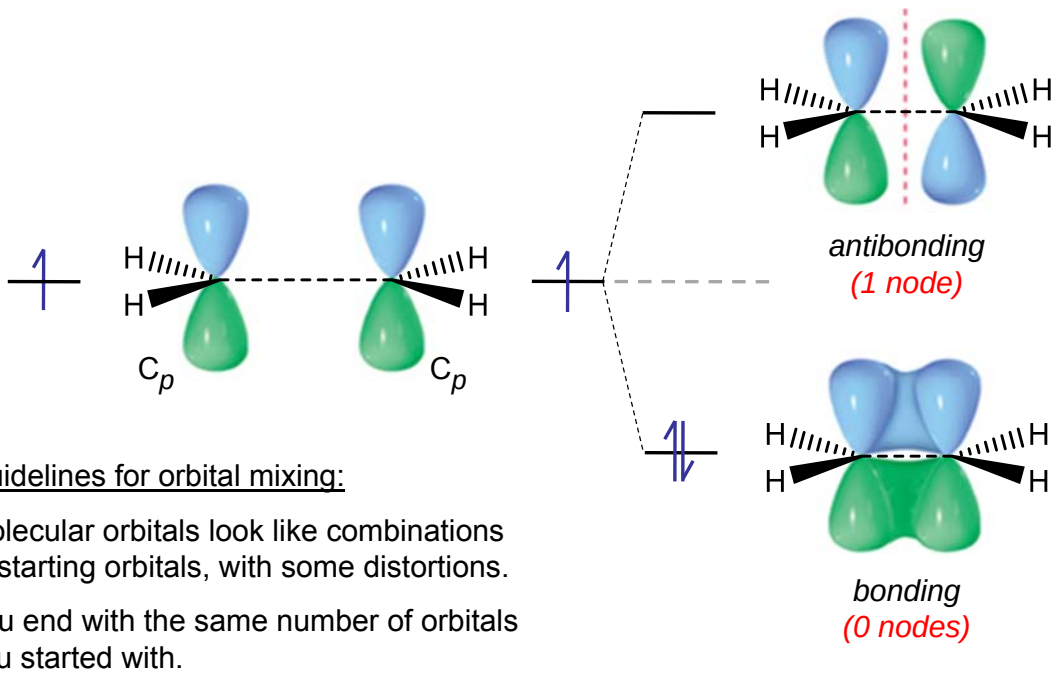
non-bonding energy level

Guidelines for orbital mixing:

Molecular orbitals look like combinations of starting orbitals, with some distortions.

You end with the same number of orbitals you started with.

Review: Constructing Molecular Orbitals by Mixing Atomic Orbitals

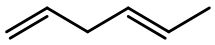


Guidelines for orbital mixing:

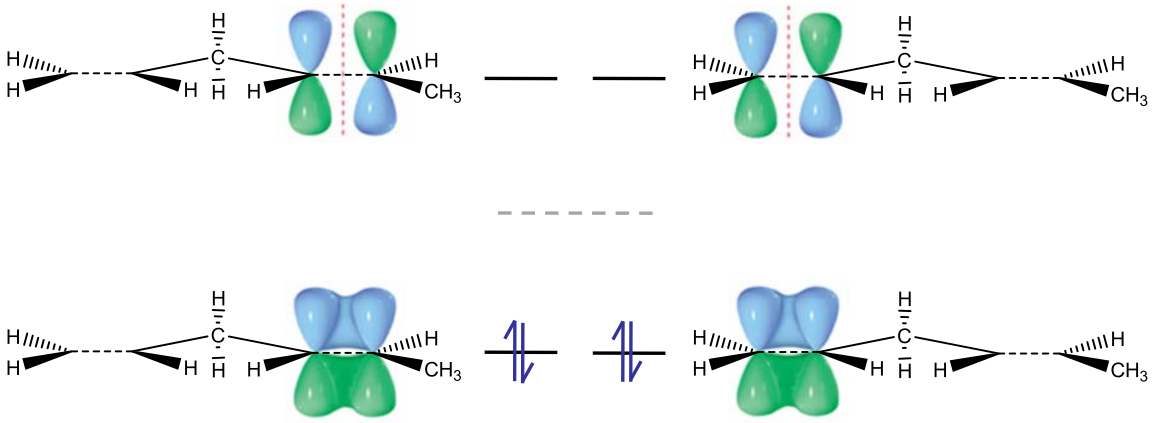
Molecular orbitals look like combinations of starting orbitals, with some distortions.

You end with the same number of orbitals you started with.

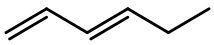
Molecular Orbitals for Non-Adjacent Double Bonds



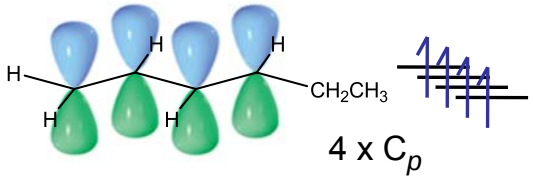
In 1,4-hexadiene, each double bond has its own separate bonding, antibonding orbitals.



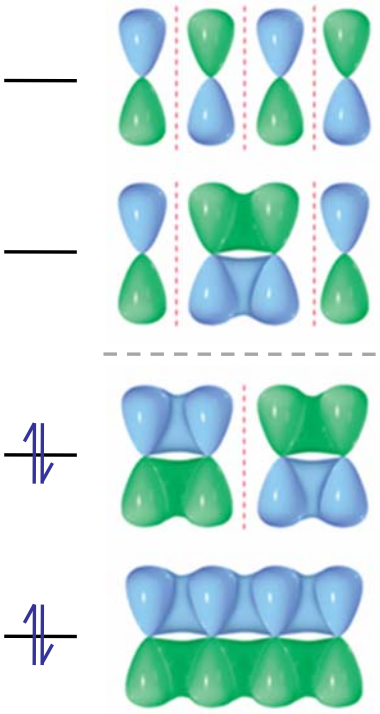
Conjugated Molecular Orbitals



In 1,3-hexadiene, all orbitals mix.



4 x C_p



Guidelines for orbital mixing:

Molecular orbitals look like combinations of starting orbitals, with some distortions.

You end with the same number of orbitals you started with.

Conjugated Molecular Orbitals

<u>More guidelines for orbital mixing:</u>

Start with zero nodes at bottom, and increase on the way up.
(Usually nodes will appear between atoms, but sometimes on atoms.)

Distribute orbitals over full energy range.

Orbital energies are ordered by number of bonding and antibonding interactions.

Molecular orbitals can be either perfectly symmetric or antisymmetric.