10.5
Classes of Dienes

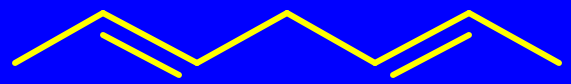
Classification of Dienes

isolated diene

conjugated diene

cumulated diene

Nomenclature



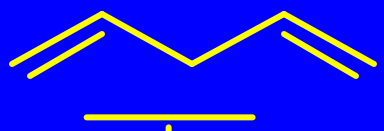
(2*E*,5*E*)-2,5-heptadiene

(2*E*,4*E*)-2,4-heptadiene

3,4-heptadiene

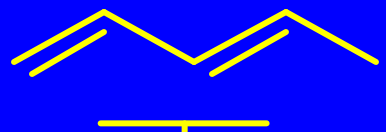
10.6
Relative Stabilities of Dienes

Heats of Hydrogenation



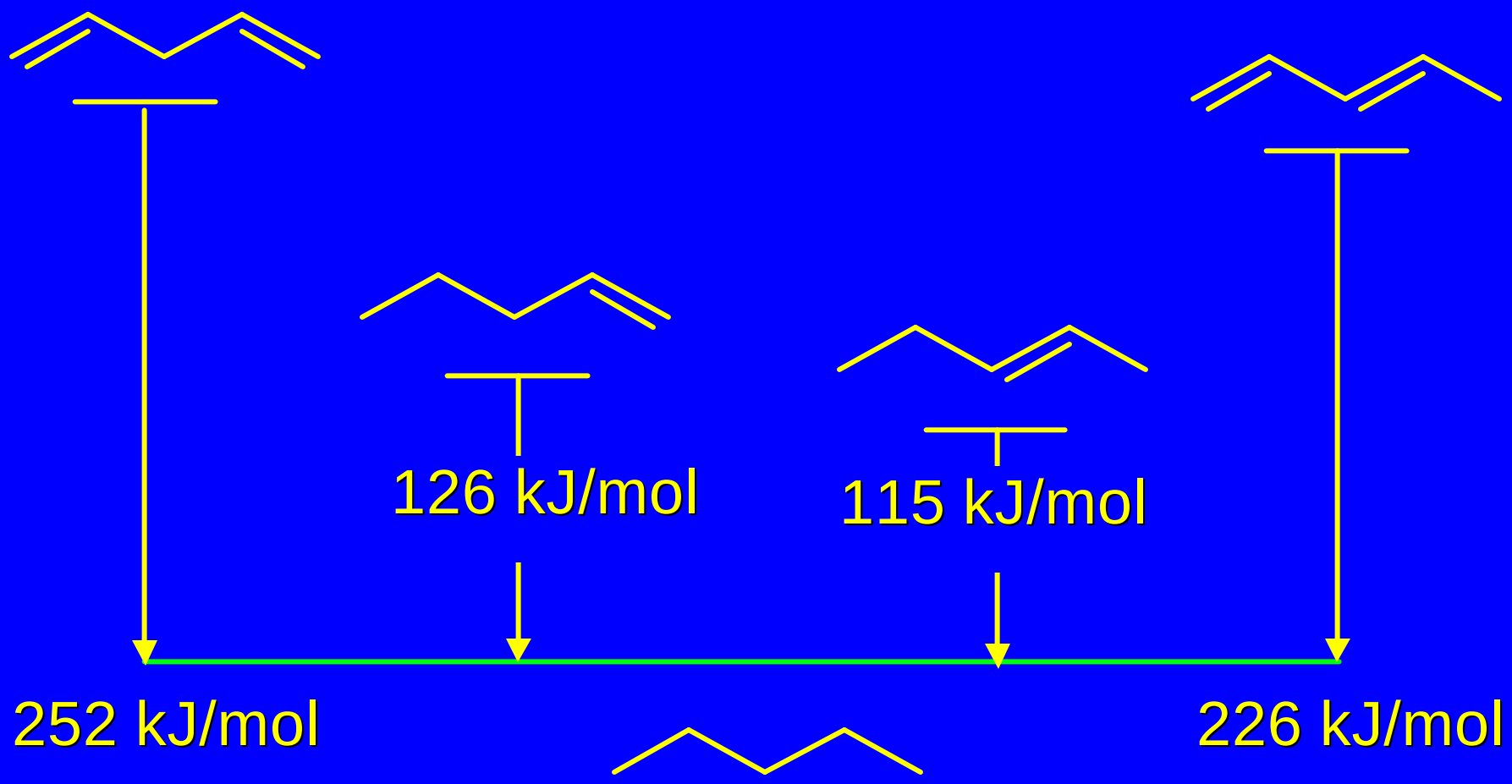
252 kJ/mol

1,3-pentadiene is 26 kJ/mol more stable than 1,4-pentadiene, but some of this stabilization is because it also contains a more highly substituted double bond

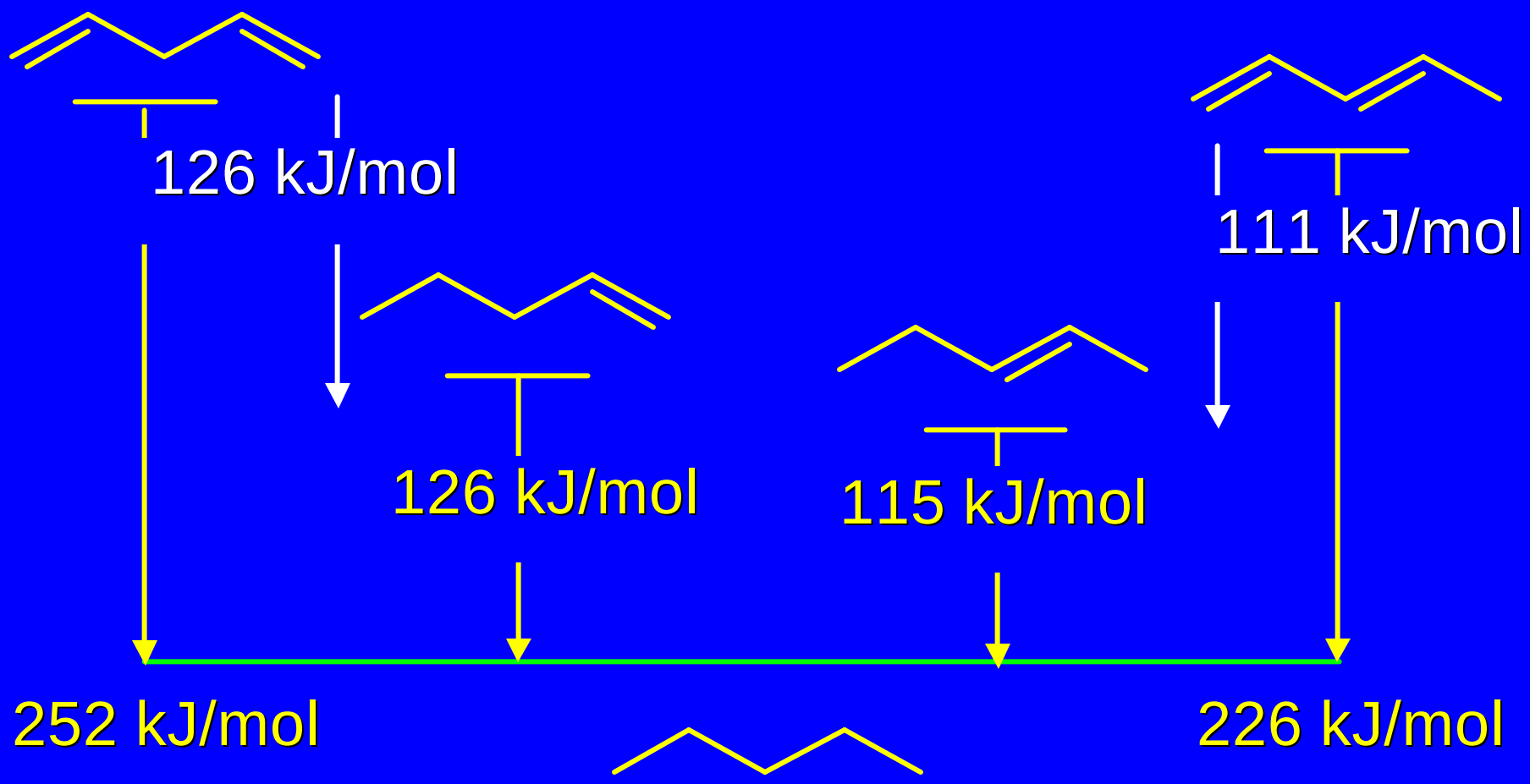


226 kJ/mol

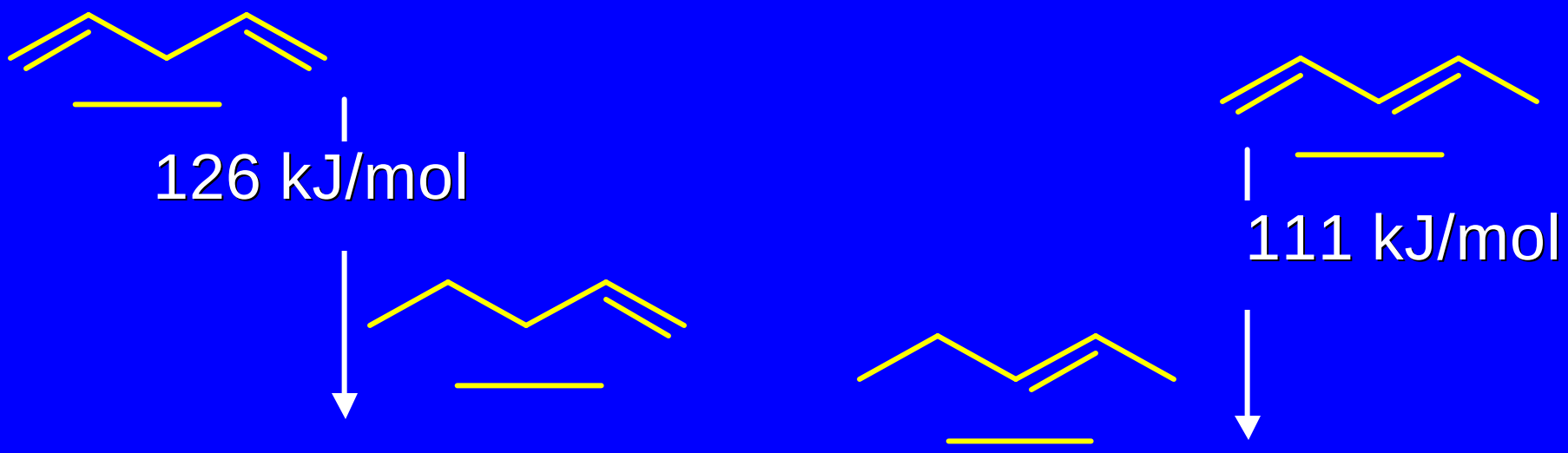
Heats of Hydrogenation



Heats of Hydrogenation

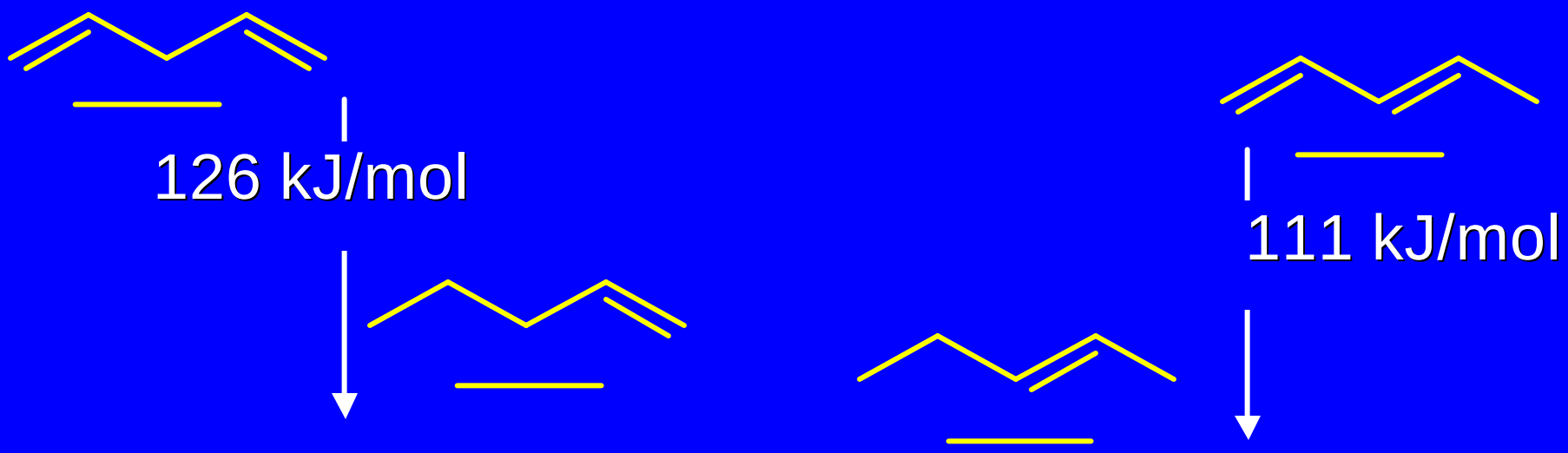


Heats of Hydrogenation



when terminal double bond is conjugated with other double bond, its heat of hydrogenation is 15 kJ/mol less than when isolated

Heats of Hydrogenation



this extra 15 kJ/mol is known by several terms

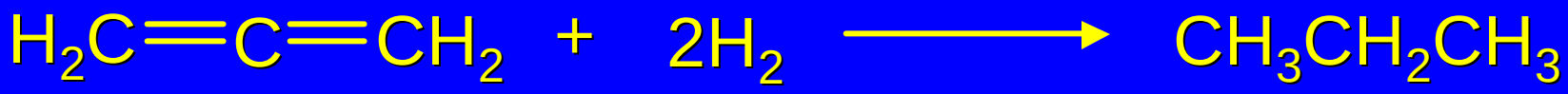
stabilization energy

delocalization energy

resonance energy

Heats of Hydrogenation

Cumulated double bonds have relatively high heats of hydrogenation

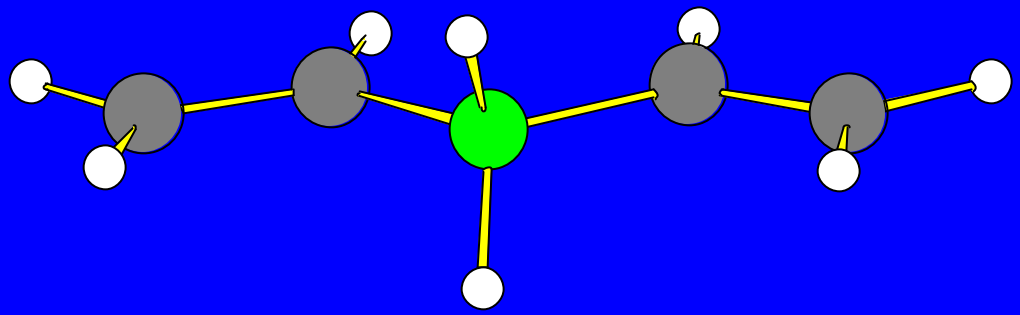


$\Delta H° = -295$ kJ

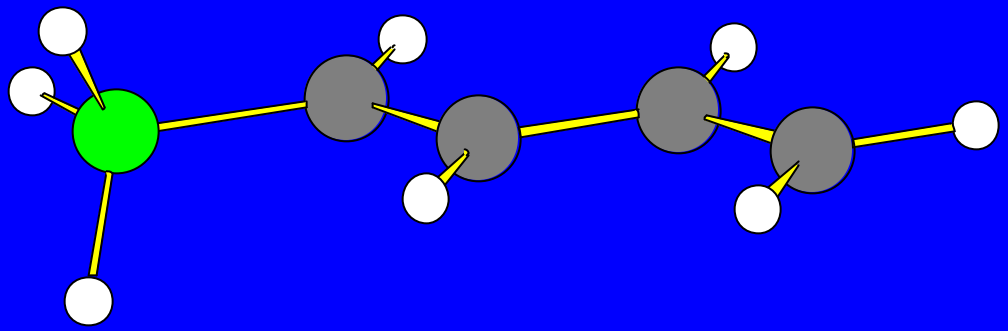
$\Delta H° = -125$ kJ

10.7
Bonding
in Conjugated Dienes

Isolated diene



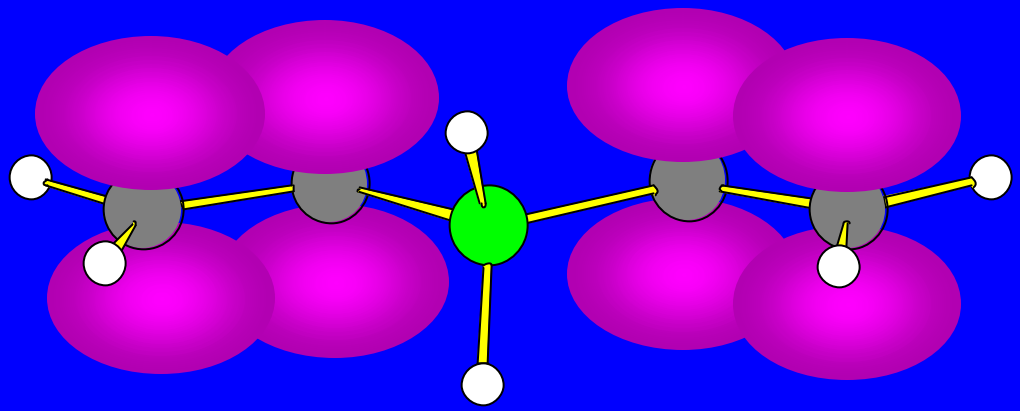
1,4-pentadiene



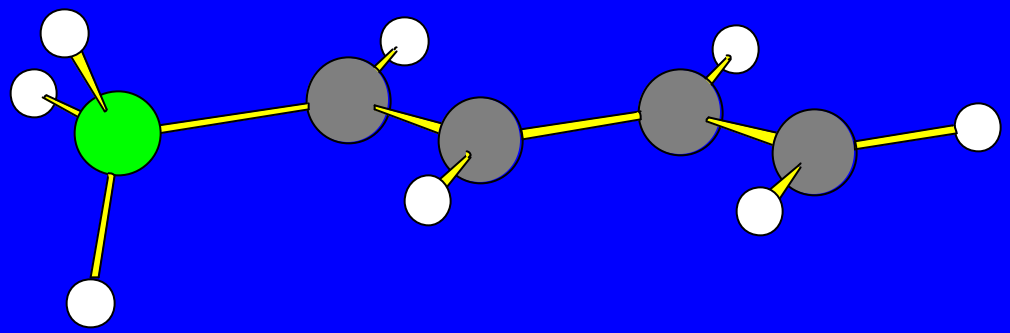
1,3-pentadiene

Conjugated diene

Isolated diene



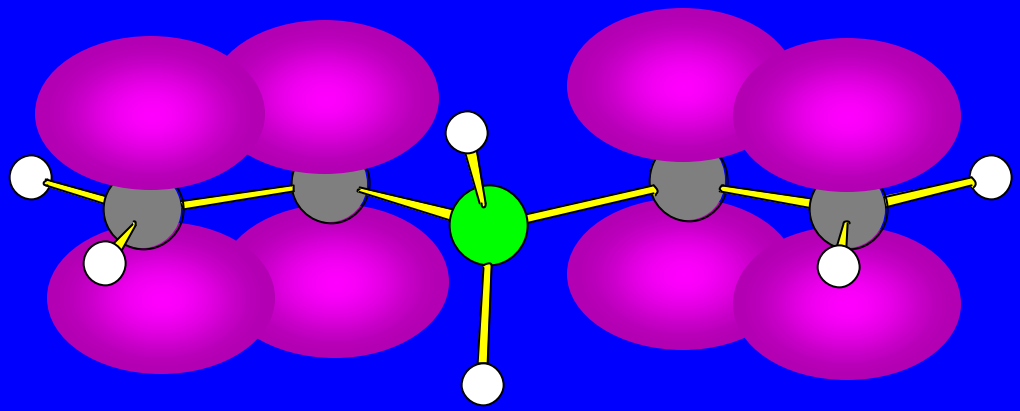
p bonds are independent of each other



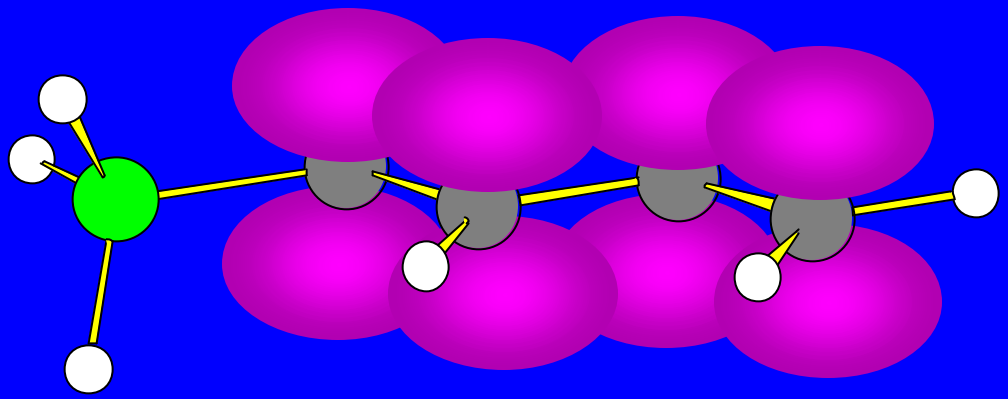
1,3-pentadiene

Conjugated diene

Isolated diene



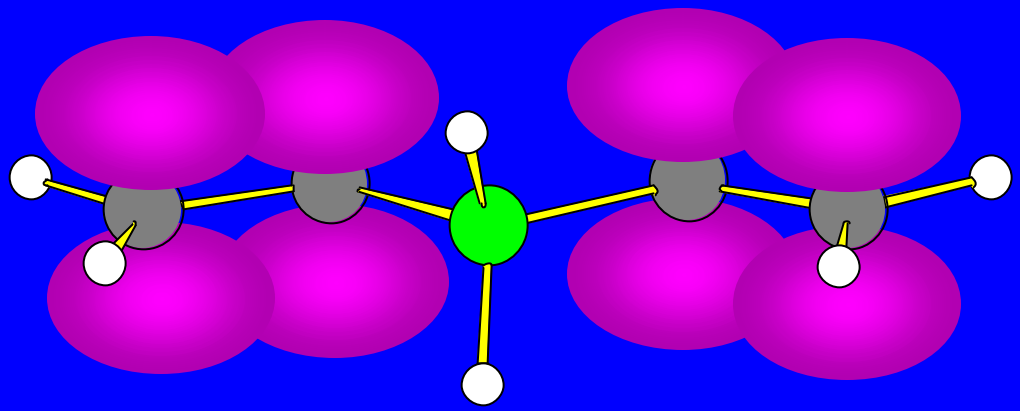
p bonds are independent of each other



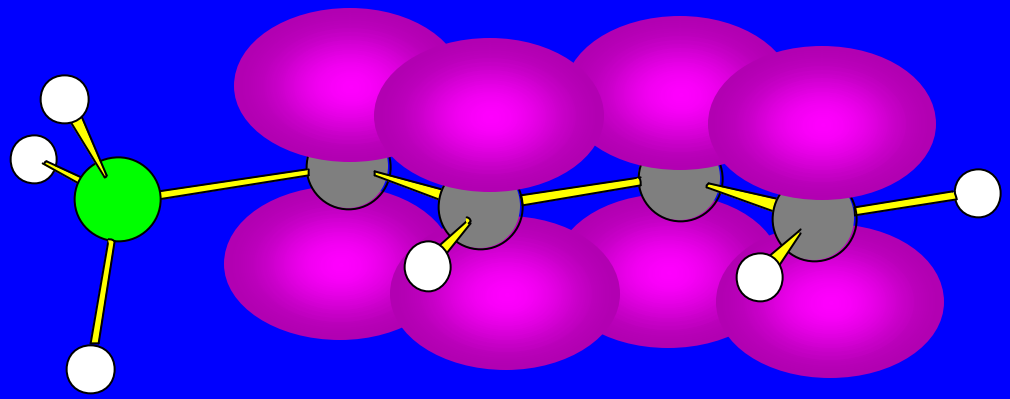
p orbitals overlap to give extended *p* bond encompassing four carbons

Conjugated diene

Isolated diene



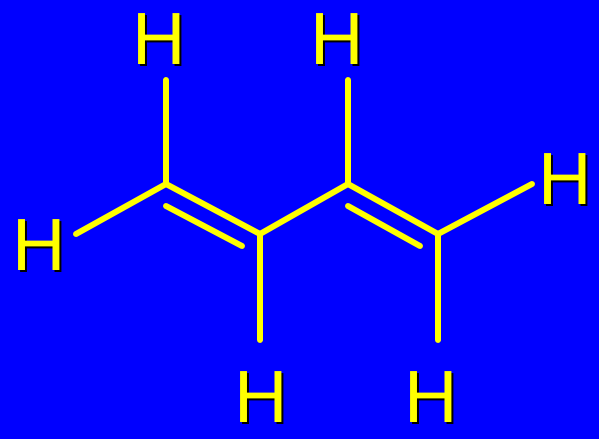
less electron delocalization; less stable



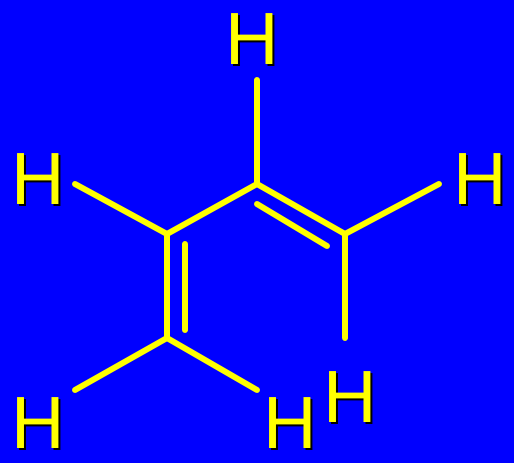
more electron delocalization; more stable

Conjugated diene

Conformations of Dienes



s-trans

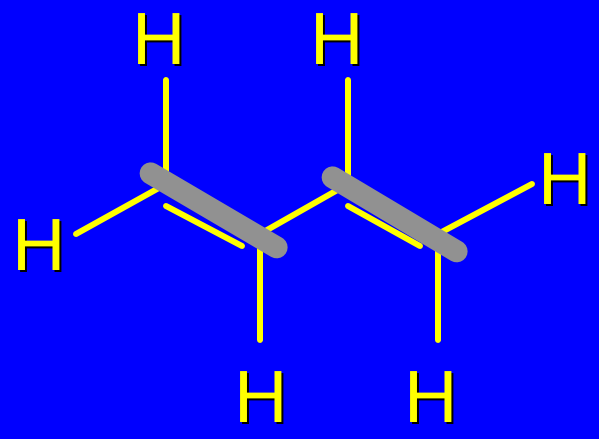


s-cis

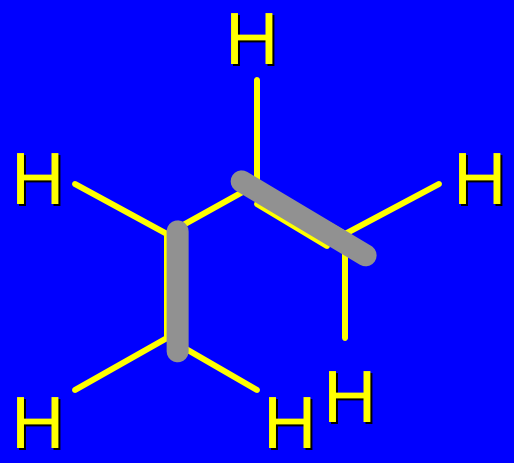
s prefix designates conformation around single bond

s prefix is lower case (different from Cahn-Ingold-Prelog *S* which designates configuration and is upper case)

Conformations of Dienes



s-trans



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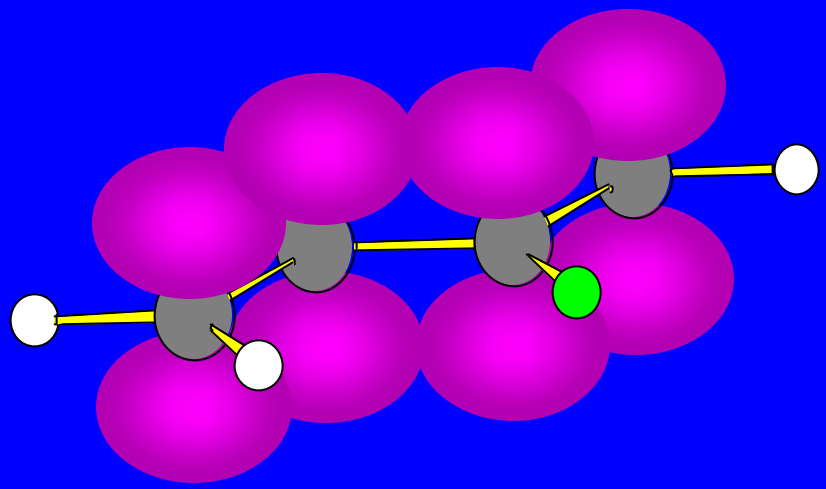
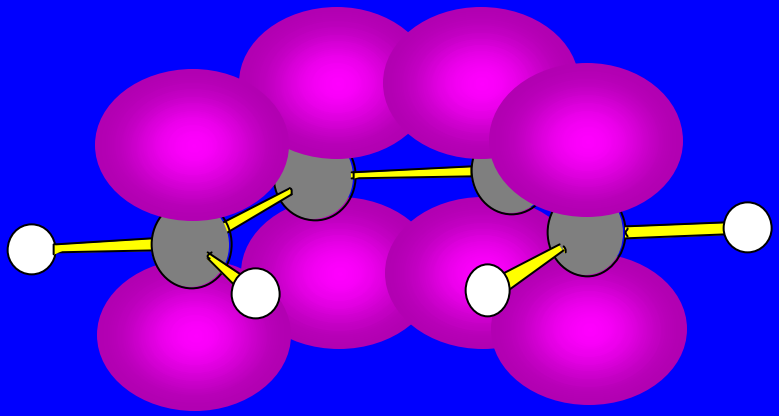
Conformations of Dienes



s-trans

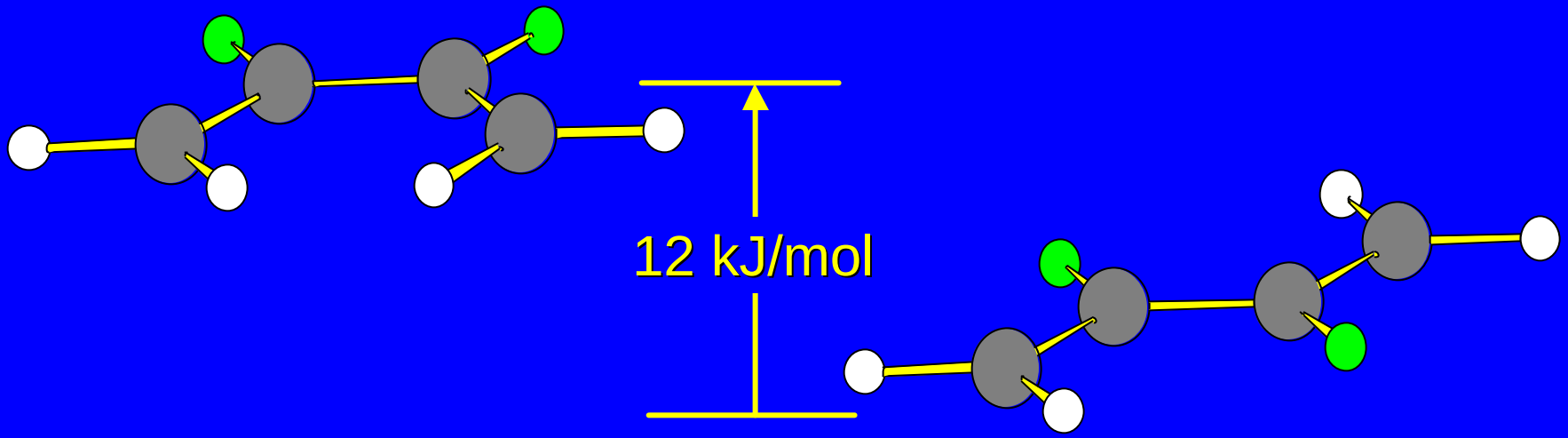


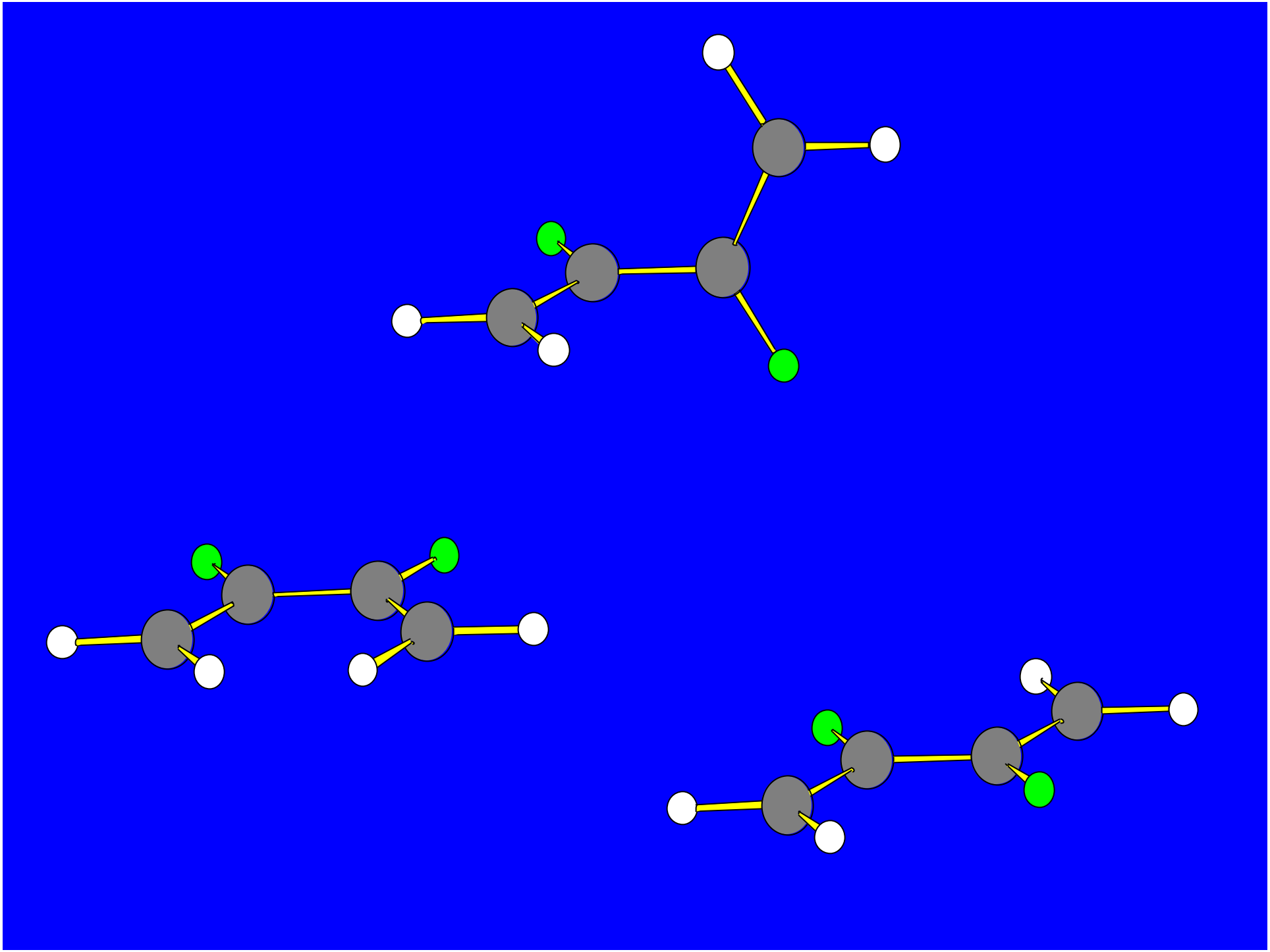
s-cis

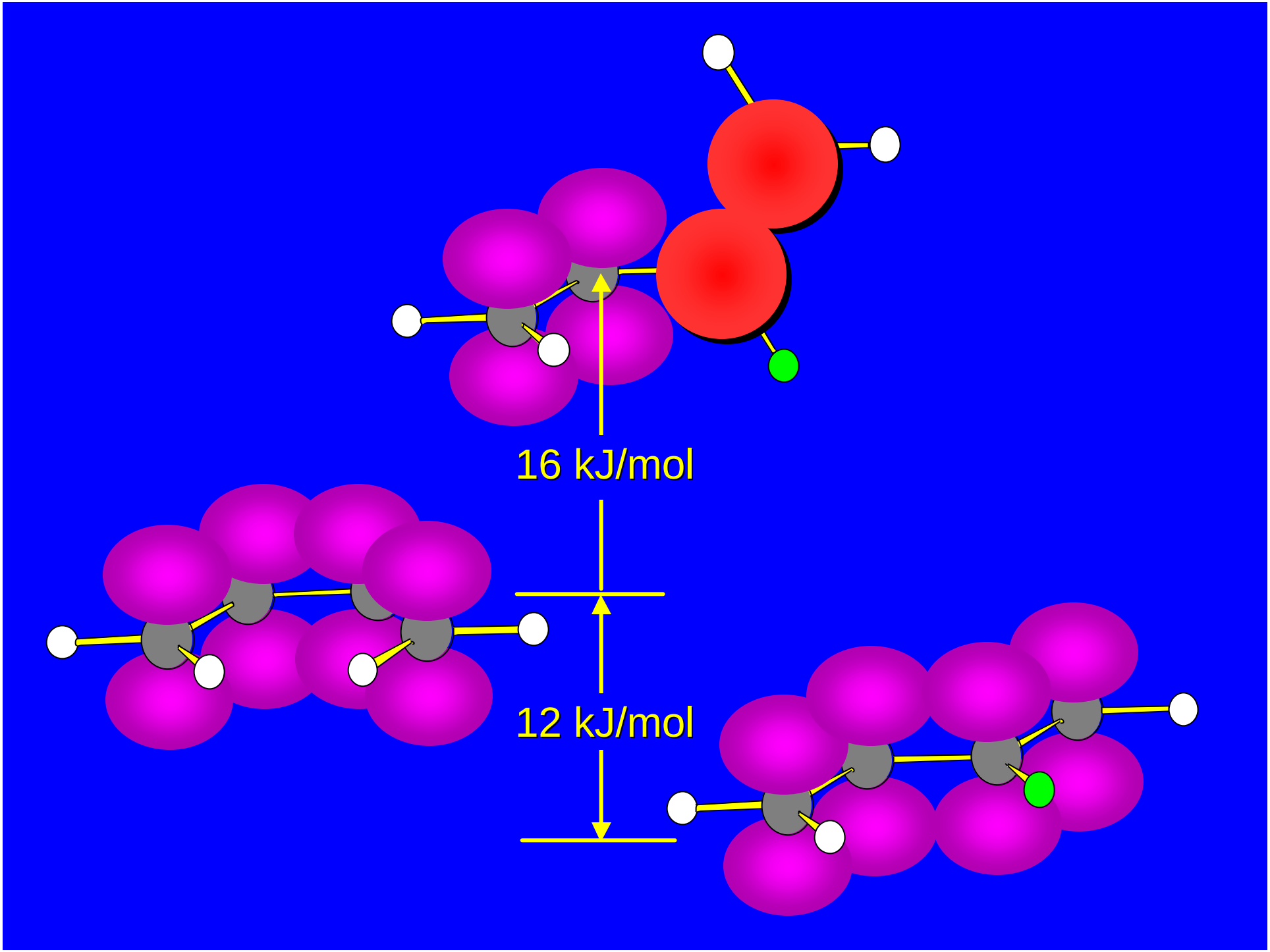
Both conformations allow electron delocalization via overlap of *p* orbitals to give extended π system

s-trans is more stable than s-cis

Interconversion of conformations requires two *p* bonds to be at right angles to each other and prevents conjugation

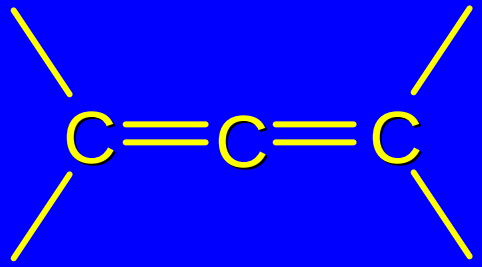





16 kJ/mol
12 kJ/mol

10.8
Bonding in Allenes

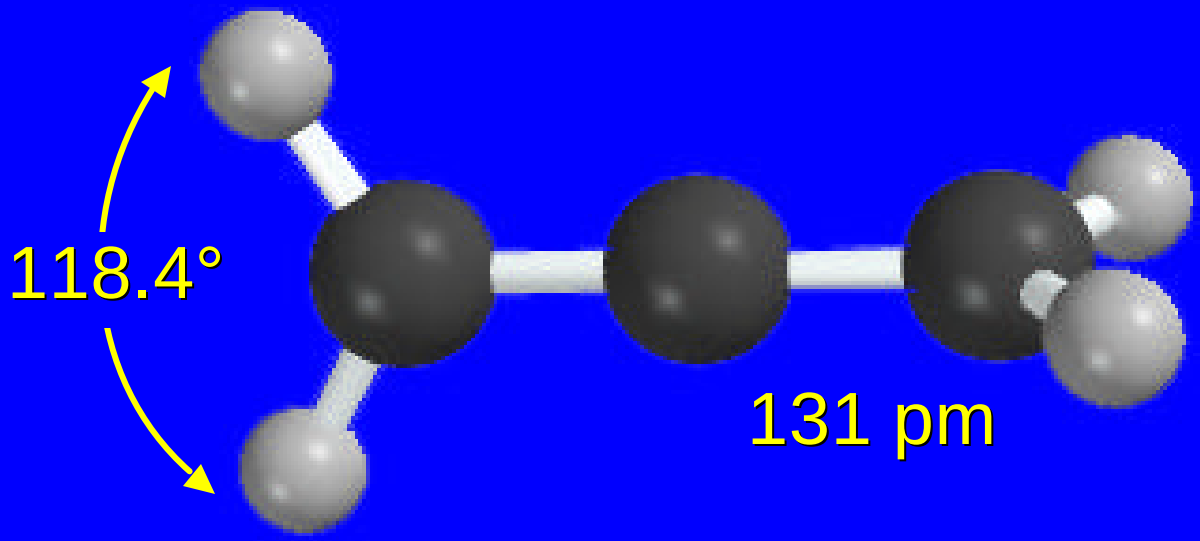
Cumulated Dienes



cumulated dienes are less stable than isolated and conjugated dienes

(see Problem 10.7 on p 375)

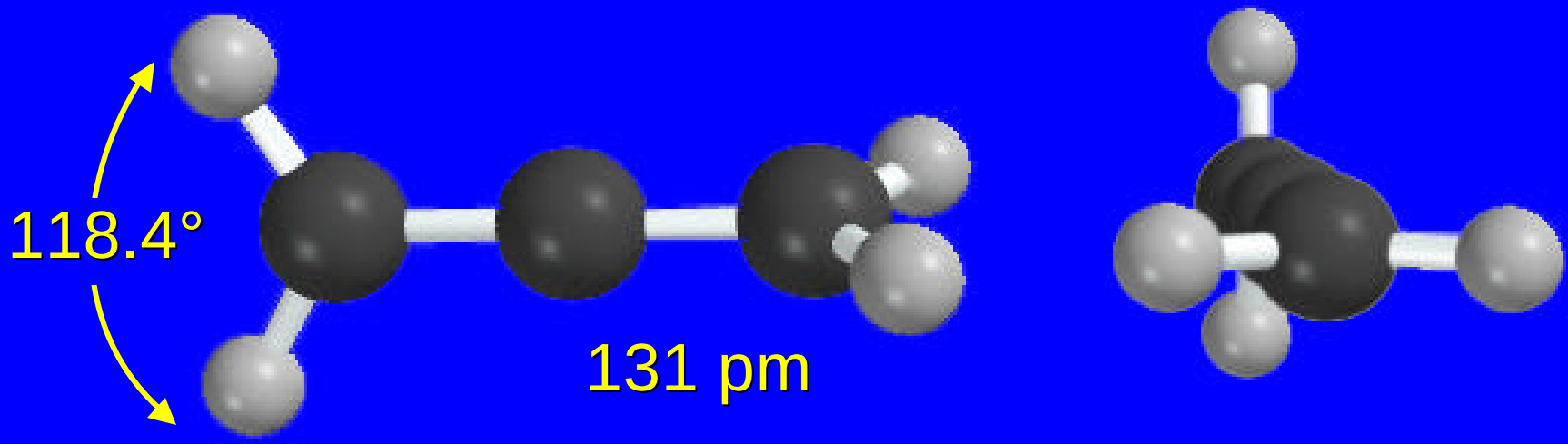
Structure of Allene



linear arrangement of carbons

nonplanar geometry

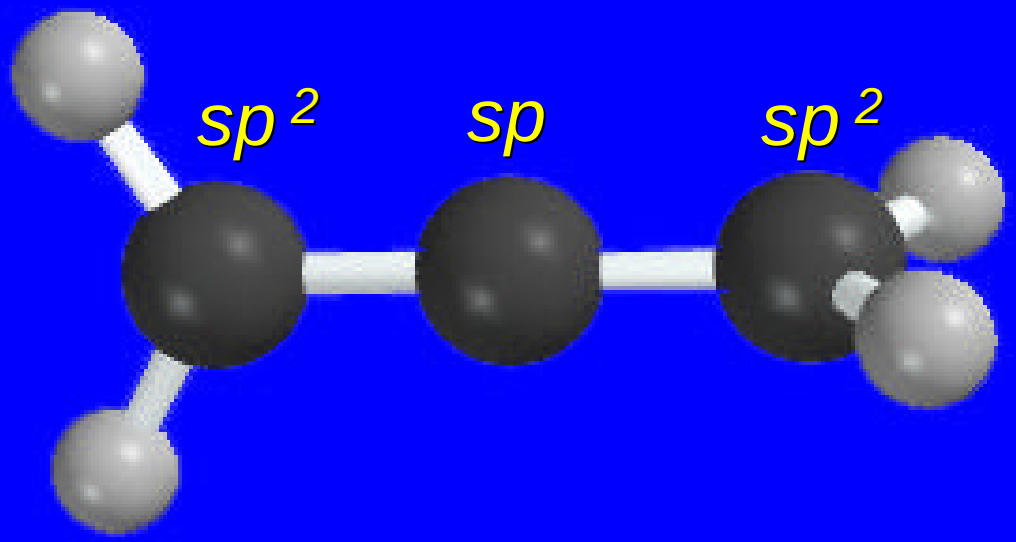
Structure of Allene



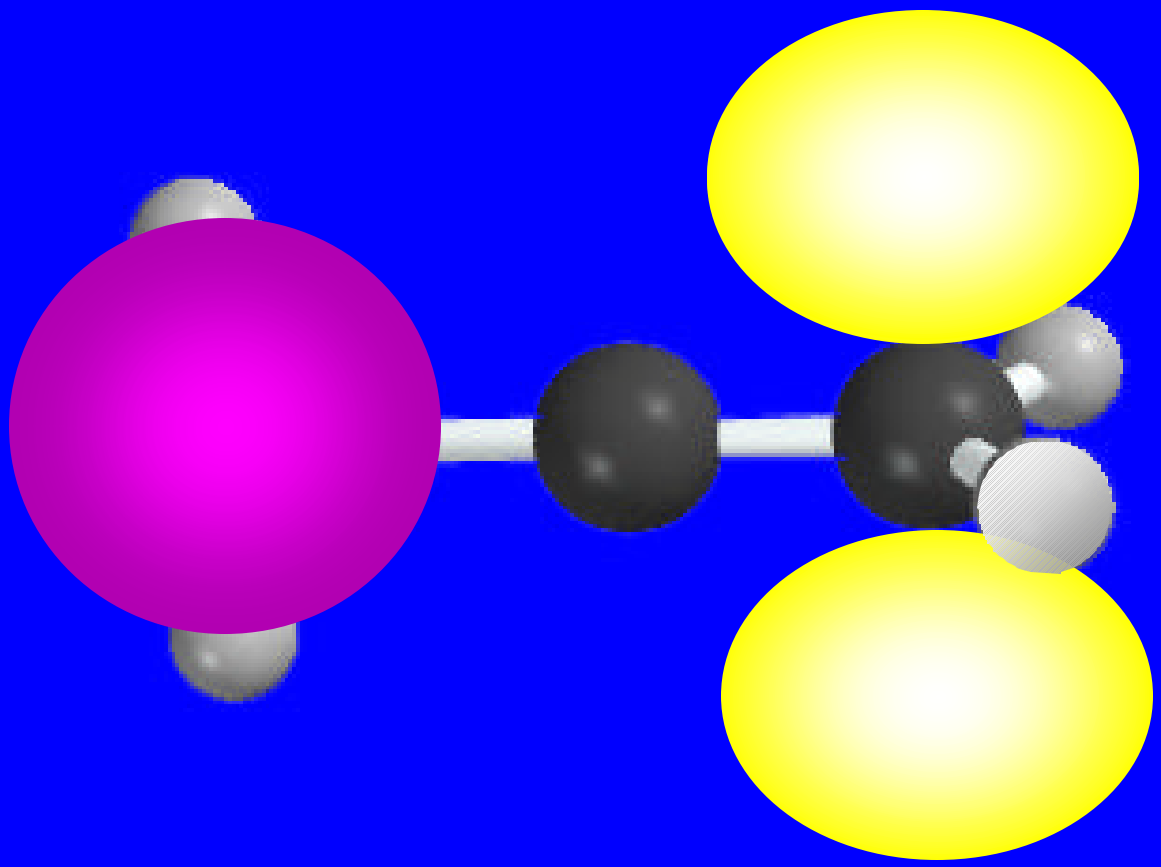
linear arrangement of carbons

nonplanar geometry

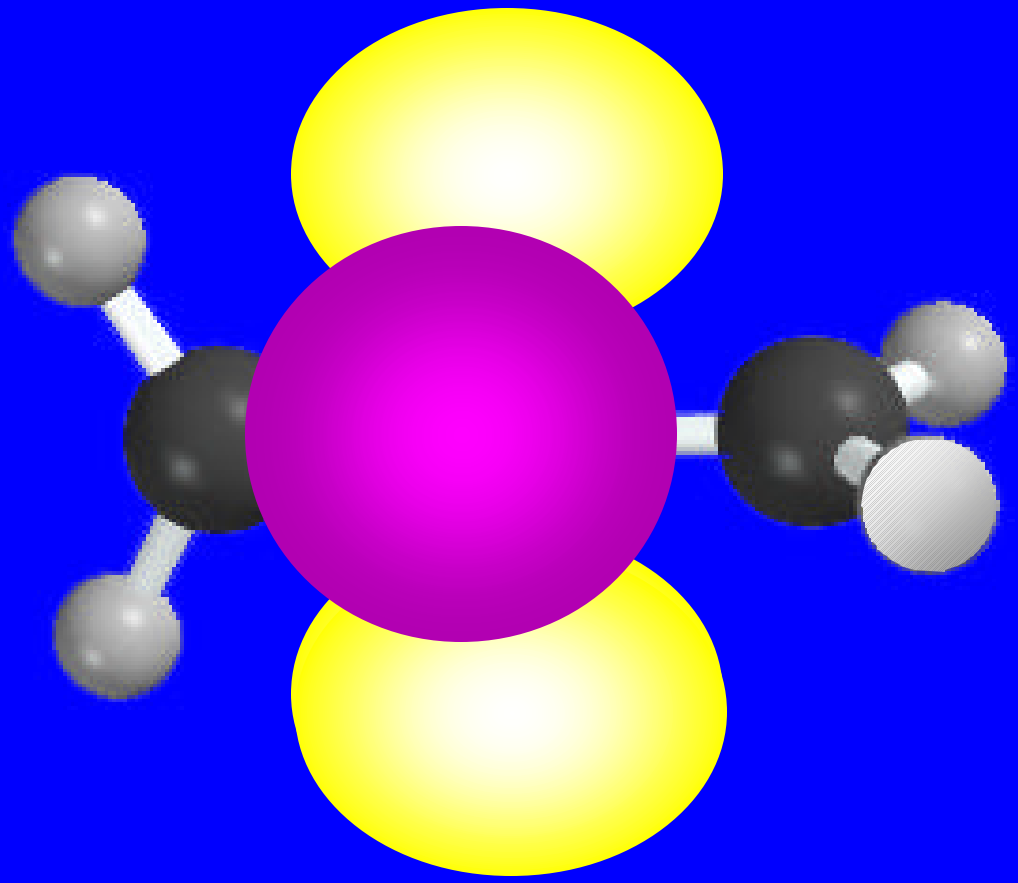
Bonding in Allene



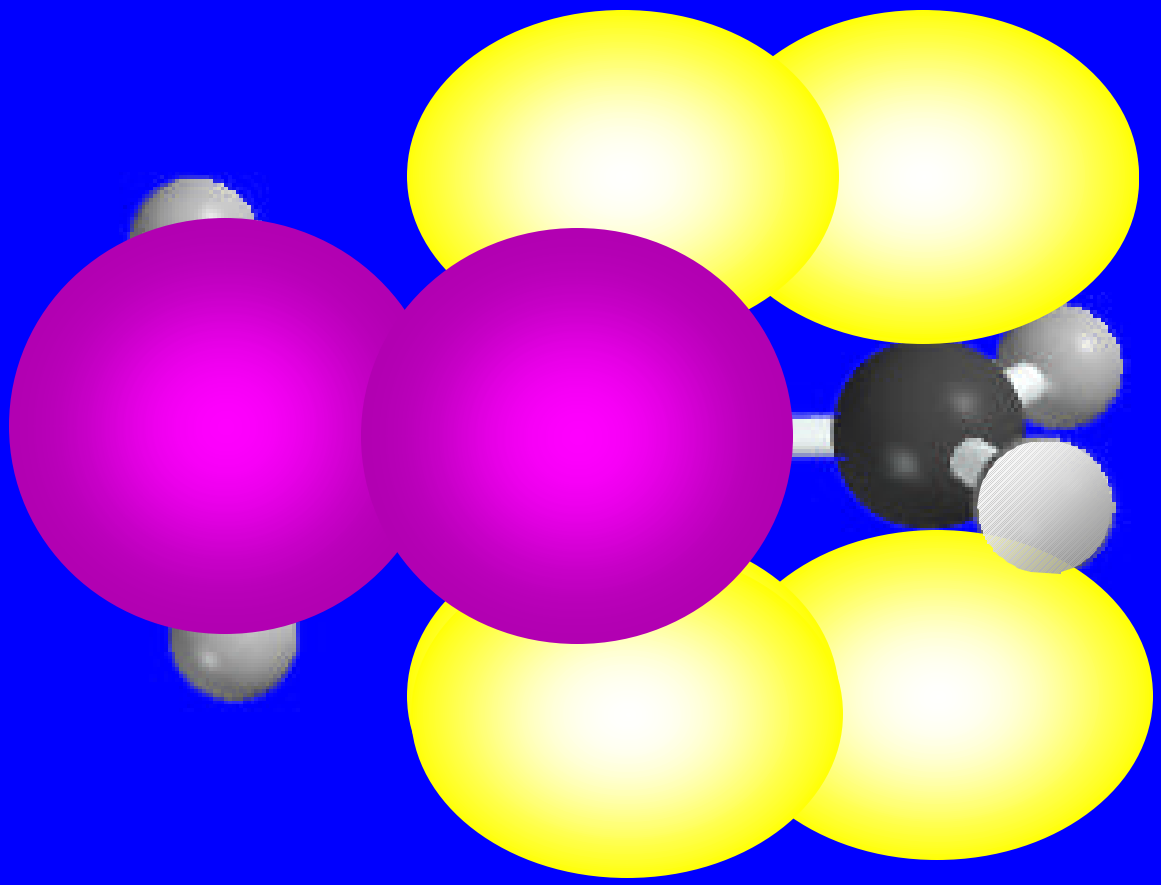
Bonding in Allene



Bonding in Allene

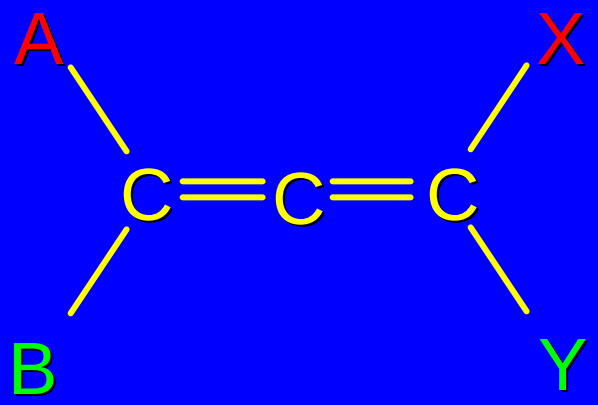


Bonding in Allene



Chiral Allenes

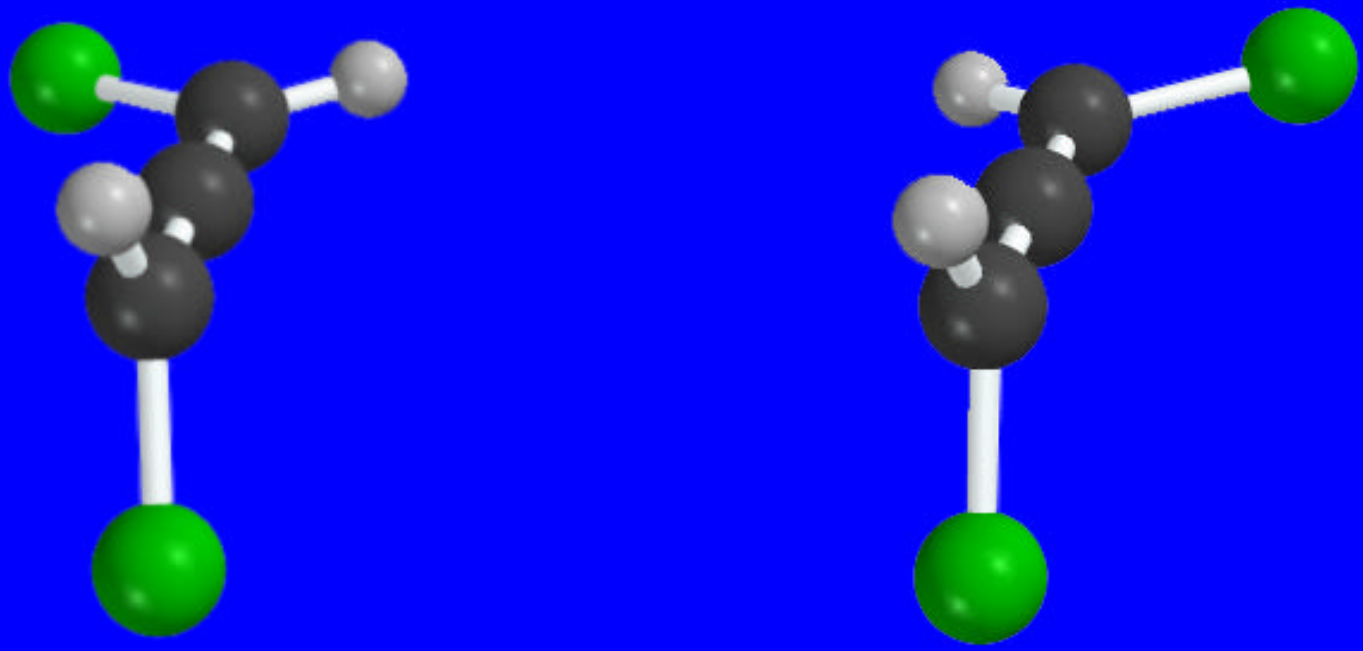
Allenes of the type shown are chiral



A ð B; X ð Y

Have a stereogenic axis

Stereogenic Axis



analogous to difference between:

a screw with a right-hand thread and one with a left-hand thread

a right-handed helix and a left-handed helix