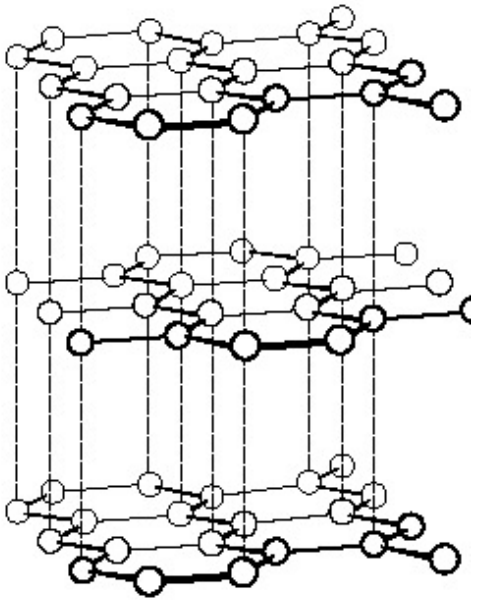
Instituto de Química – USP

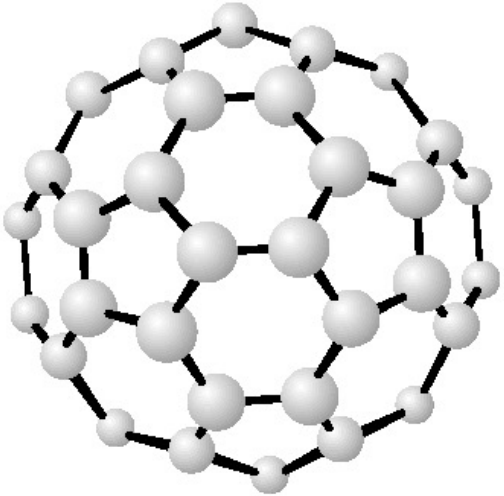
QFL 0450

Química Geral e Orgânica para Biomedicina

Ligações Químicas Localizadas

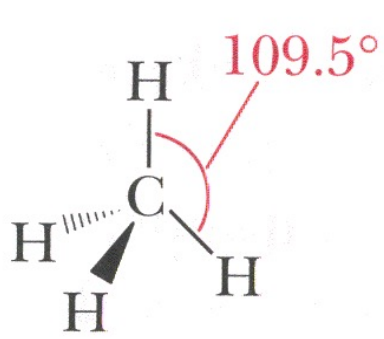


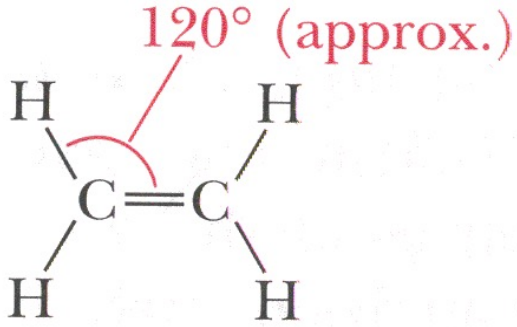
graphite

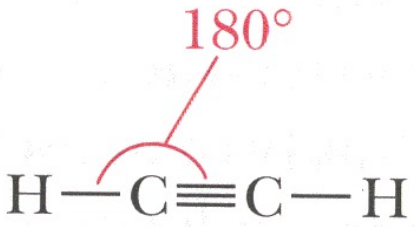


Fullerene

Exemplos de Moléculas Orgânicas







O modelo de ligação química deve explicar as informações acima!

Teoria da Ligação de Valência (VB)

Ligação química localizada:

Dois orbitais atômicos se sobrepõe (cada um contendo um elétron), gerando dois orbitais moleculares:

a) Orbital ligante: tem uma energia menor do que a dos dois orbitais atômicos.

b) Orbital anti-ligante: tem uma energia maior. Permanece vazio no estado fundamental.

Combinação de dois OA 1s

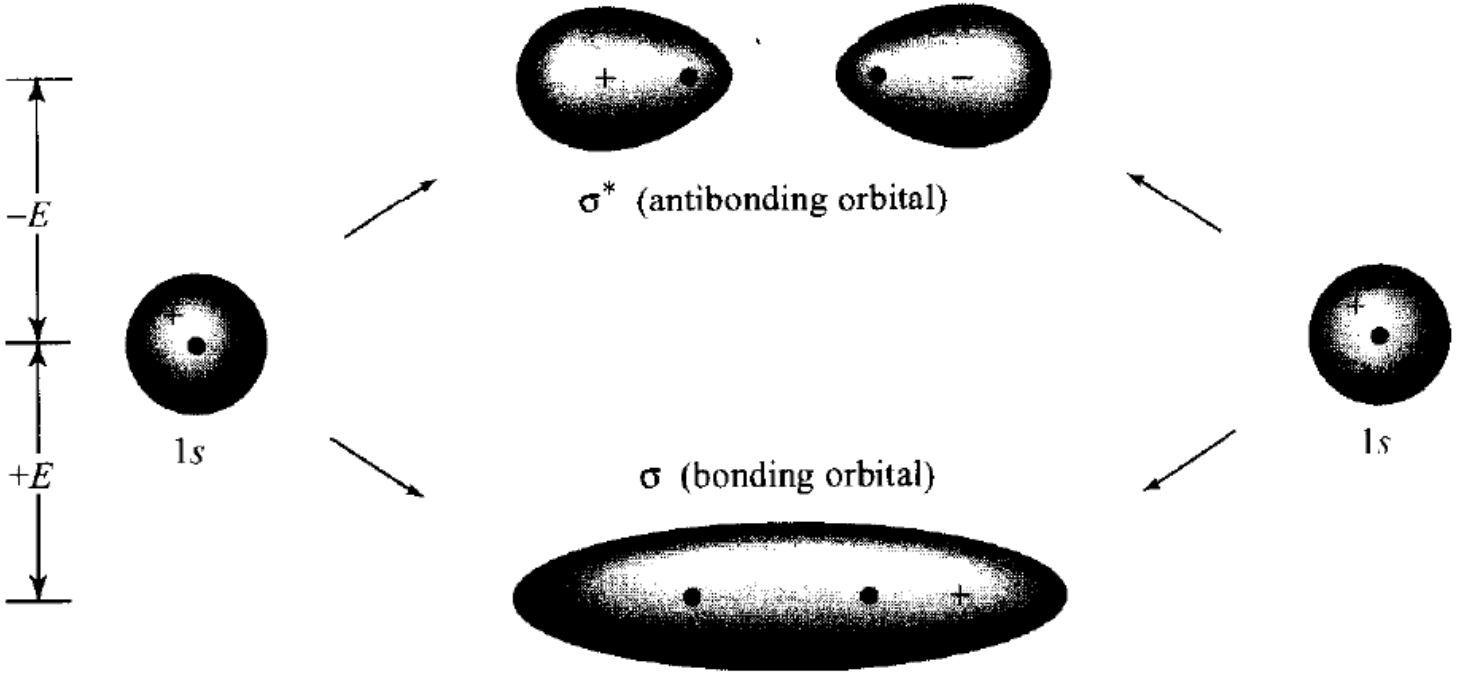
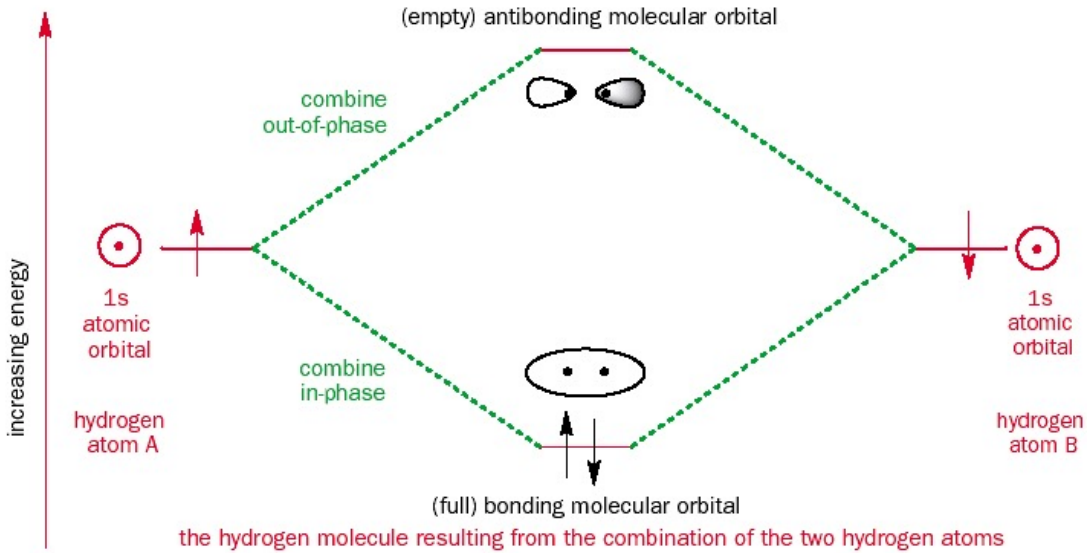


FIGURE 1.2 Overlap of two 1*s* orbitals gives rise to a σ and a σ* orbital.

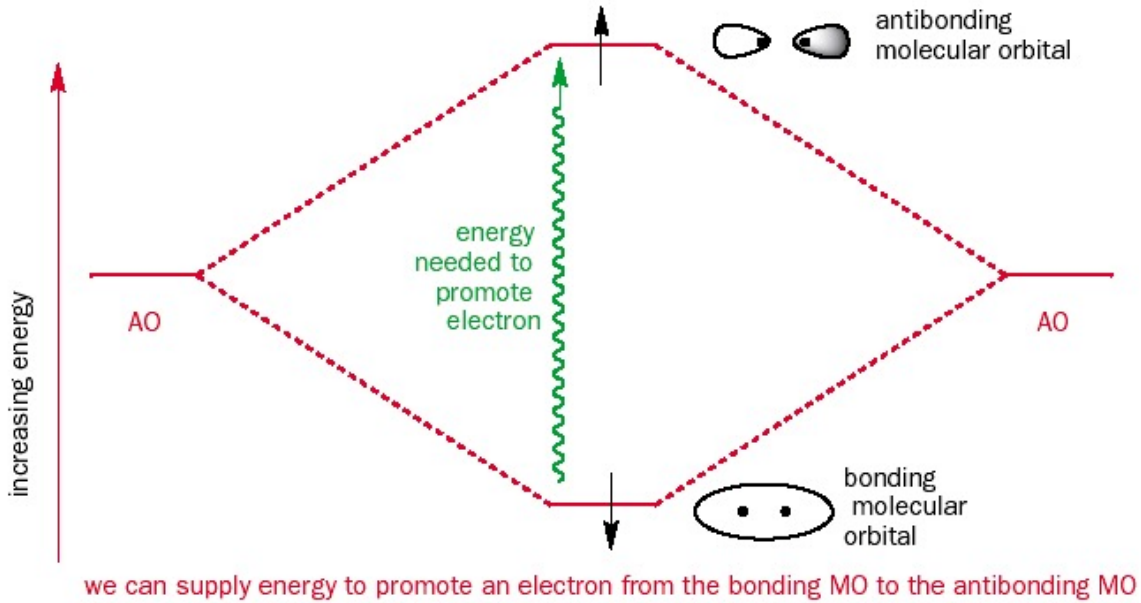
Molécula de hidrogênio



Ordem de Ligação (número de ligações entre dois átomos):

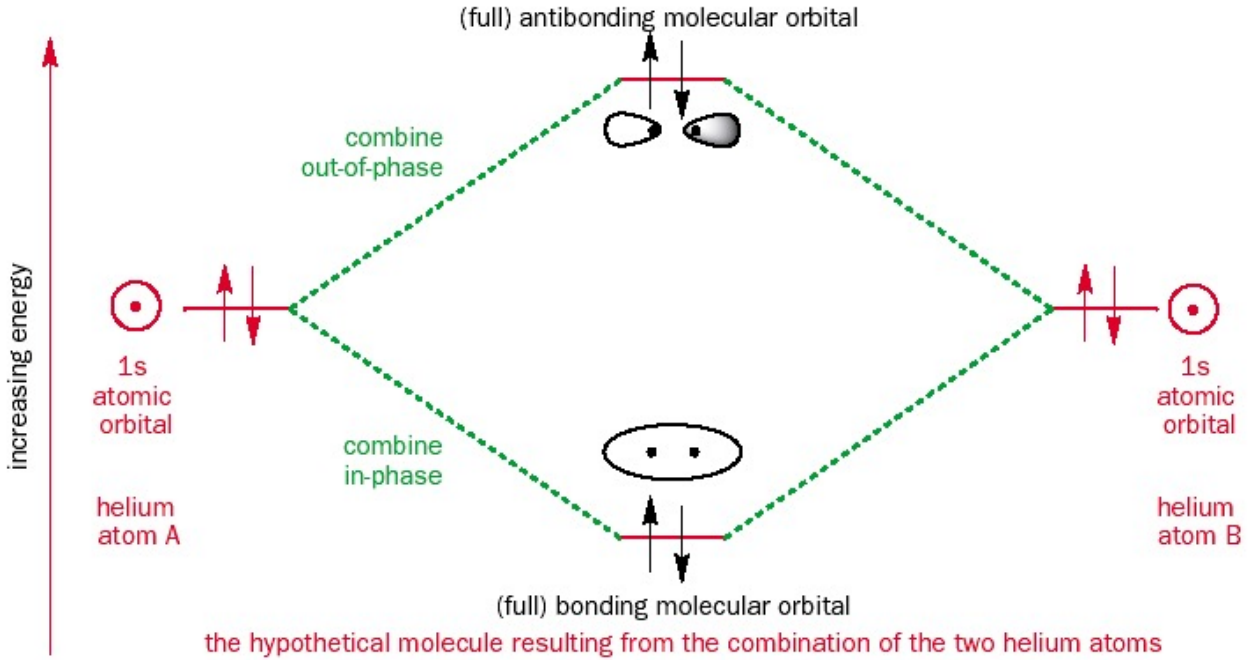
$$\text{bond order} = \frac{(\text{no. of electrons in bonding MOs}) - (\text{no. of electrons in antibonding MOs})}{2}$$

Ruptura da Molécula de Hidrogênio



Calcule a ordem de ligação

Hipotética molecular diatômica do Hélio



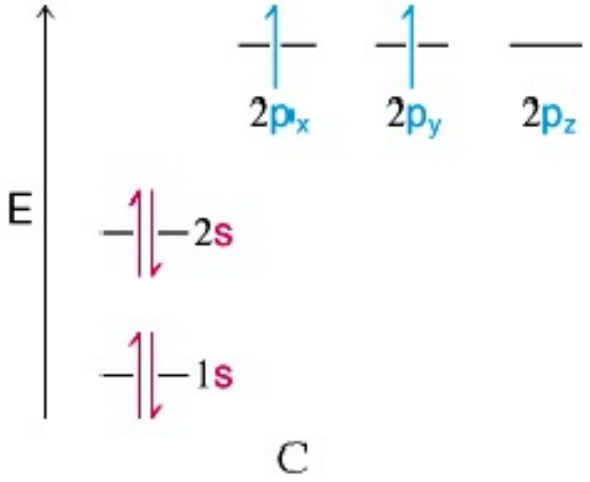
Calcule a ordem de ligação

Hibridização de orbitais

Configuração Eletrônica dos Átomos no Estado Fundamental

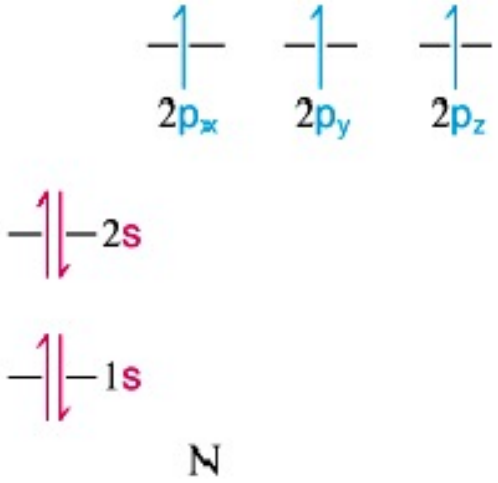
C (nº atômico: 6):

$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$



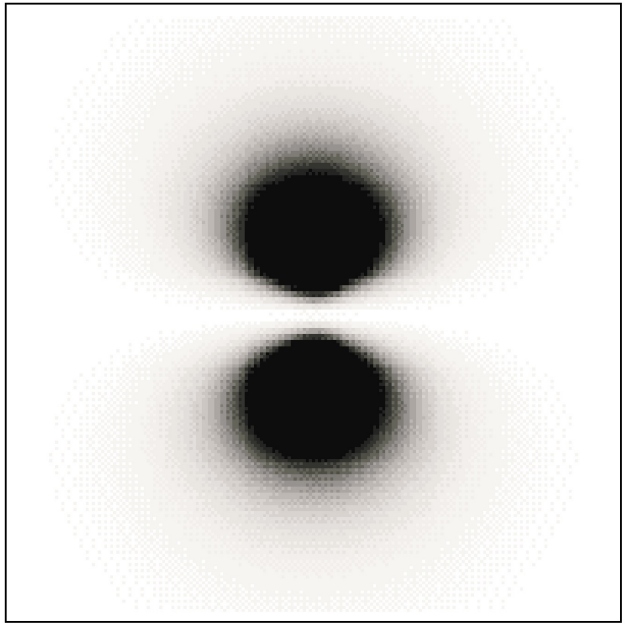
N (nº atômico: 7):

$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$

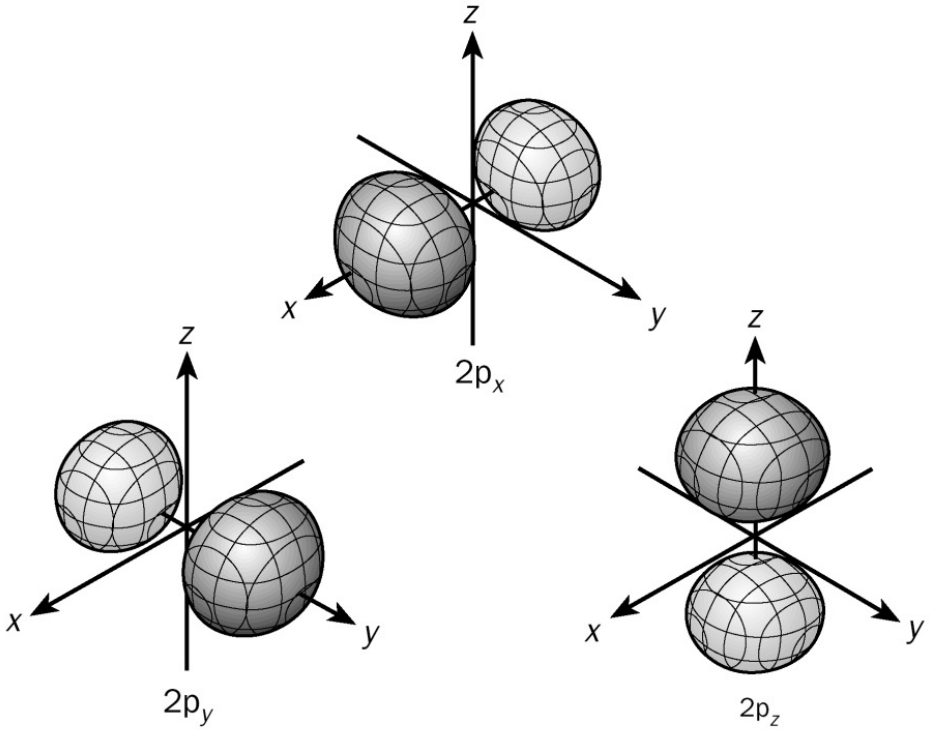


Fatos importantes

i) Os orbitais $2p_x$, $2p_y$, $2p_z$ estão orientados em ângulos de 90°.



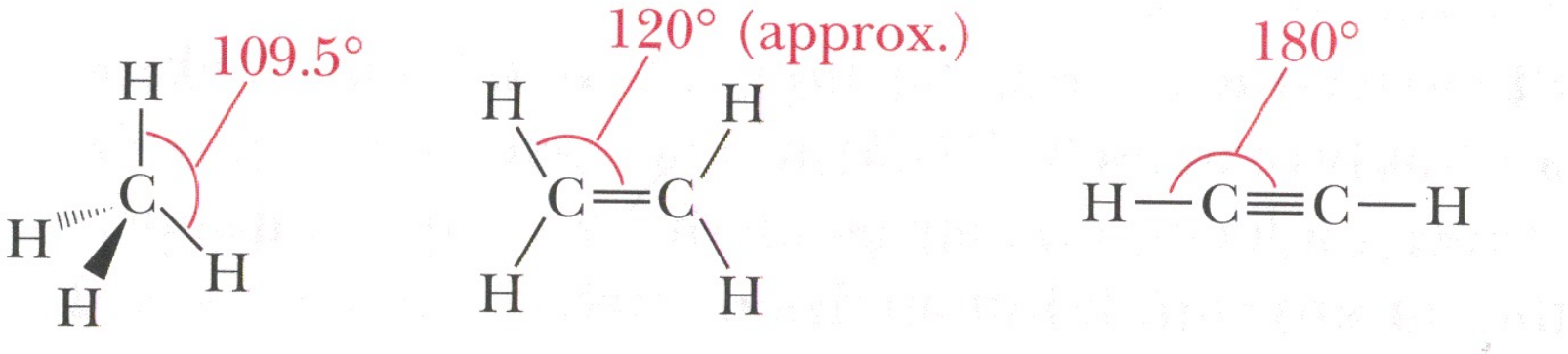
density plot of 2p orbital



three-dimensional plot of the 2p orbitals

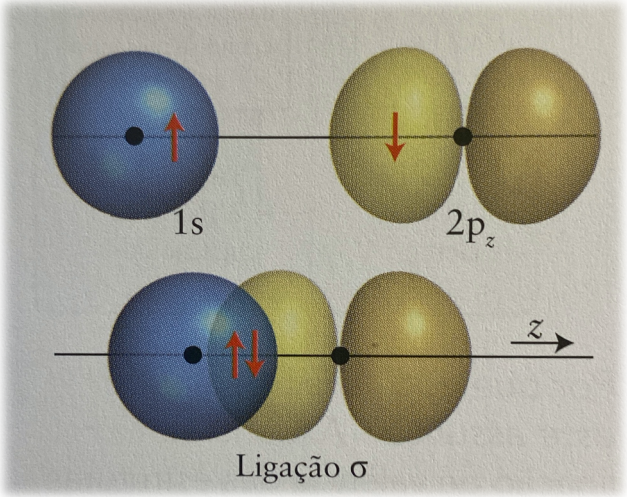
Fatos importantes

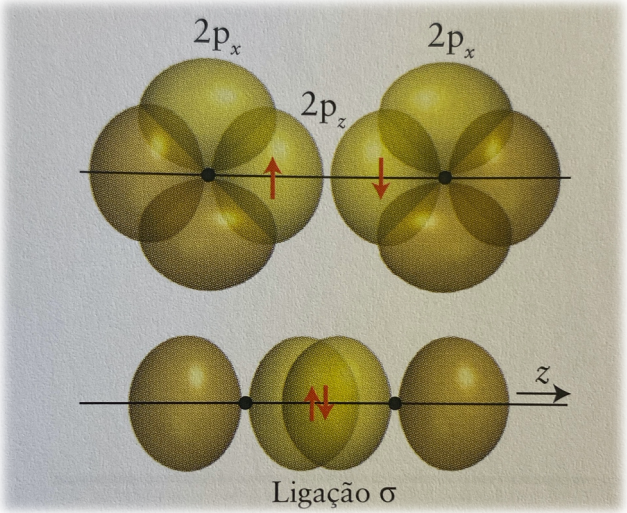
ii) Dado experimental: raramente são encontrados ângulos de 90° em moléculas orgânicas. Exemplos:

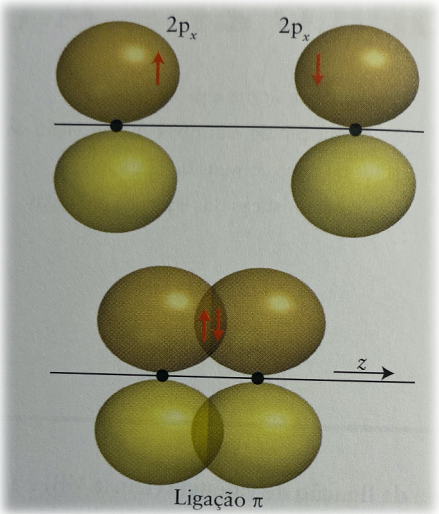


Fatos importantes

iii) Superposição de orbitais atômicos gera ligações do tipo σ e π





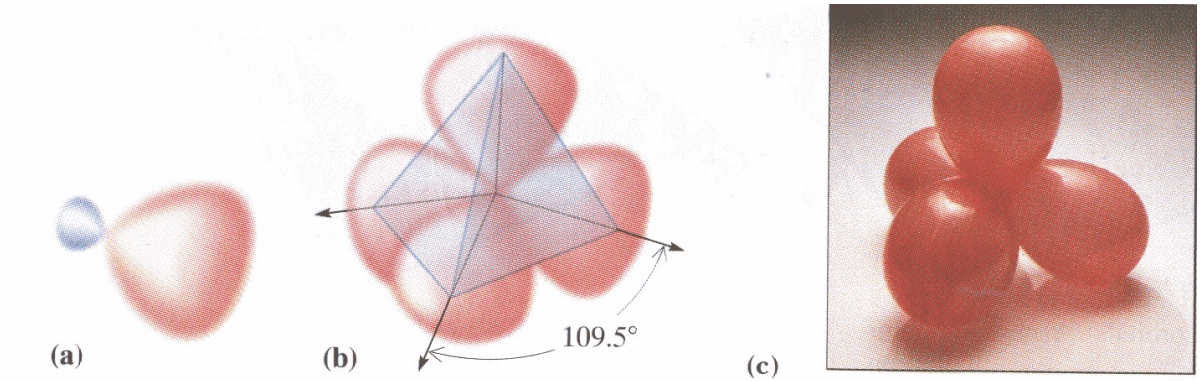


Orbitais híbridos sp^3

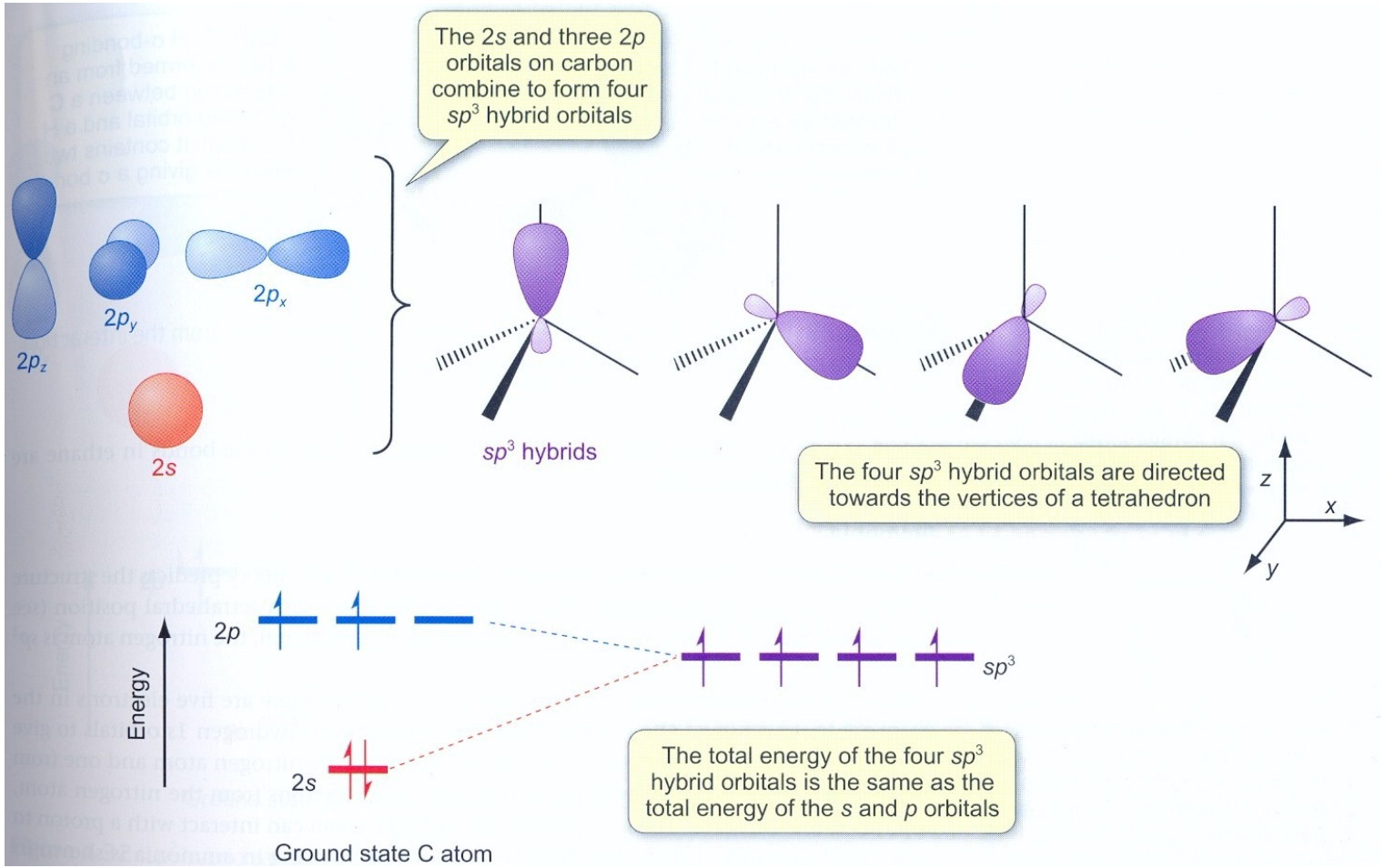
i) Combinação de um orbital atômico s e de três orbitais atômicos p formam quatro orbitais sp^3.

ii) Os quatro orbitais sp^3 têm energia equivalente.

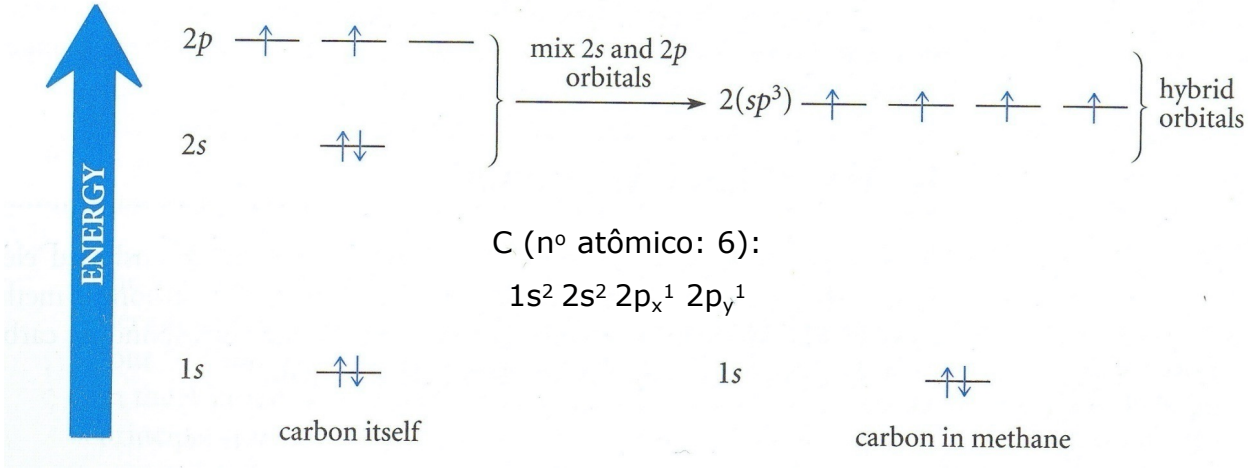
iii) ângulos de ligação de aproximadamente 109.5 ° .



Orbitais híbridos sp^3

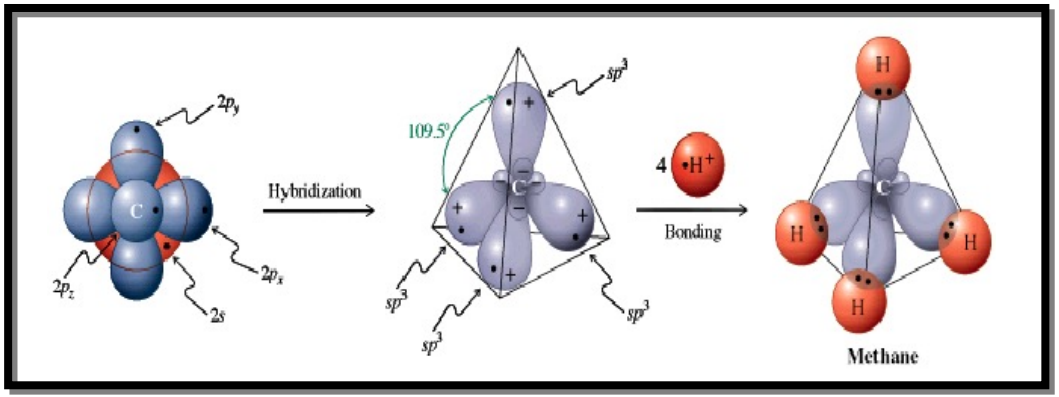


Metano

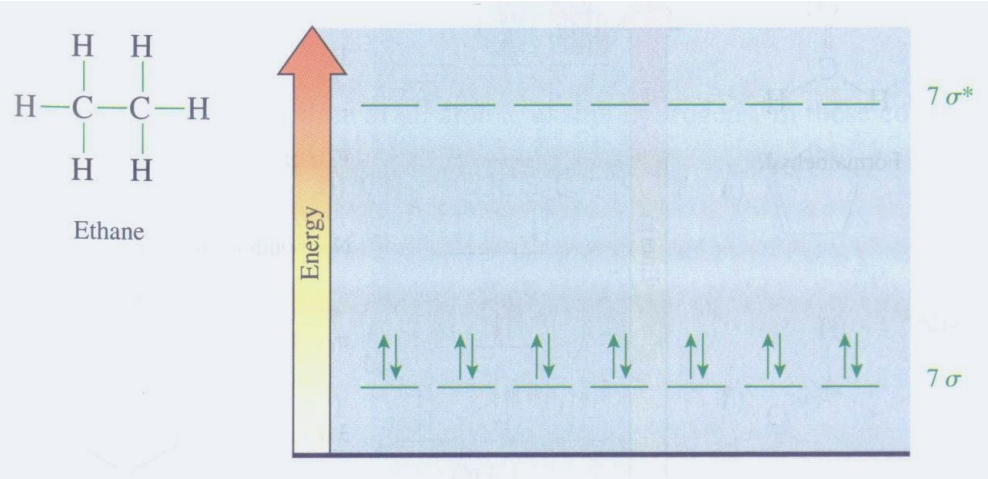


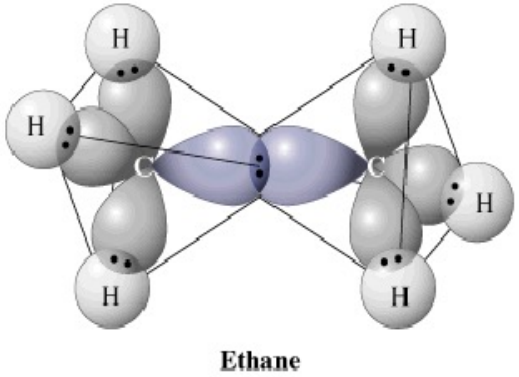
C (nº atômico: 6):

$1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$



Etano





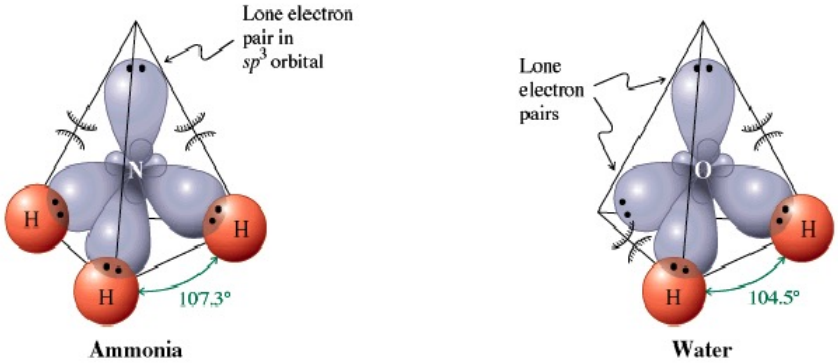
Ethane

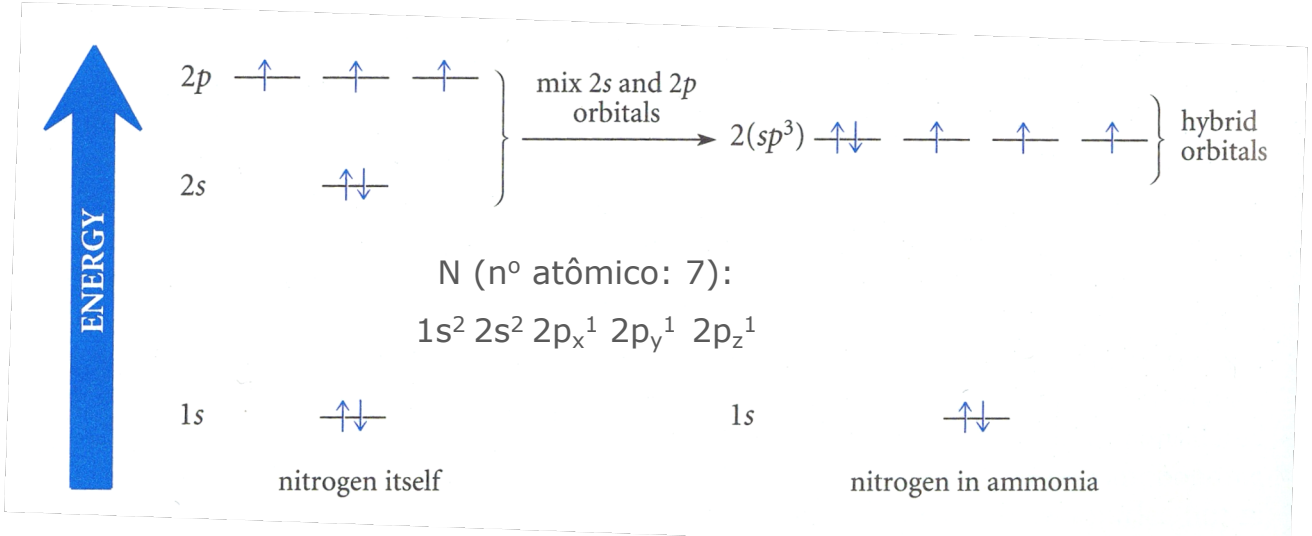
O carbono forma ligações fortes com ele mesmo e com outros elementos, ao contrário do oxigênio, nitrogênio e silício:

Ligação O-O: 34 Kcal mol^{-1}

Ligação N-O: 39 Kcal mol^{-1}

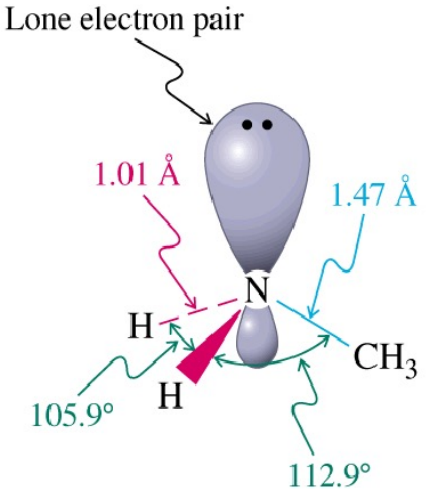
Amônia e água

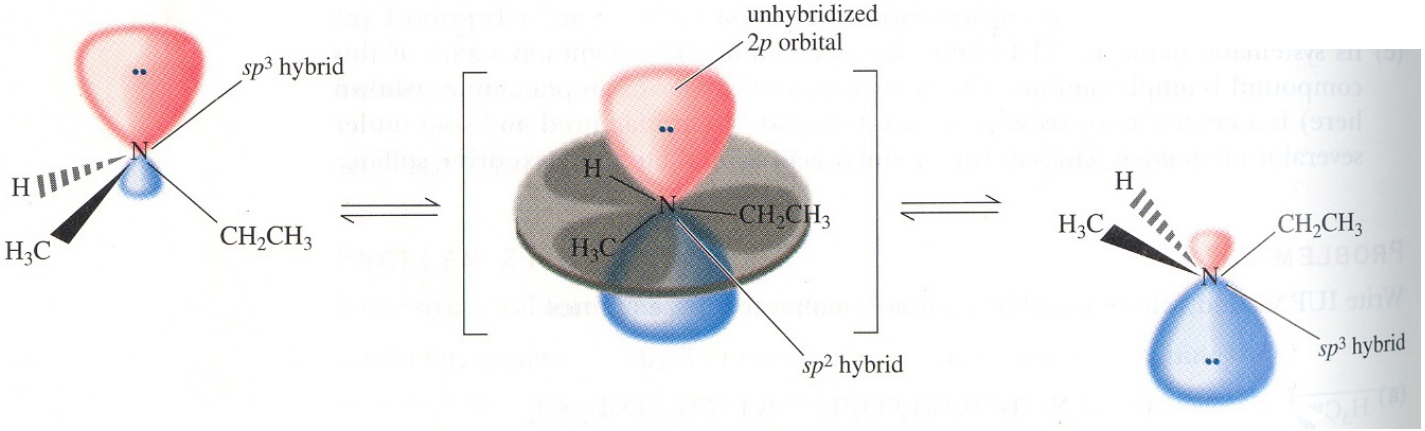




Metilamina

Para a amônia ocorrem
2.10^{11} inversões por segundo!



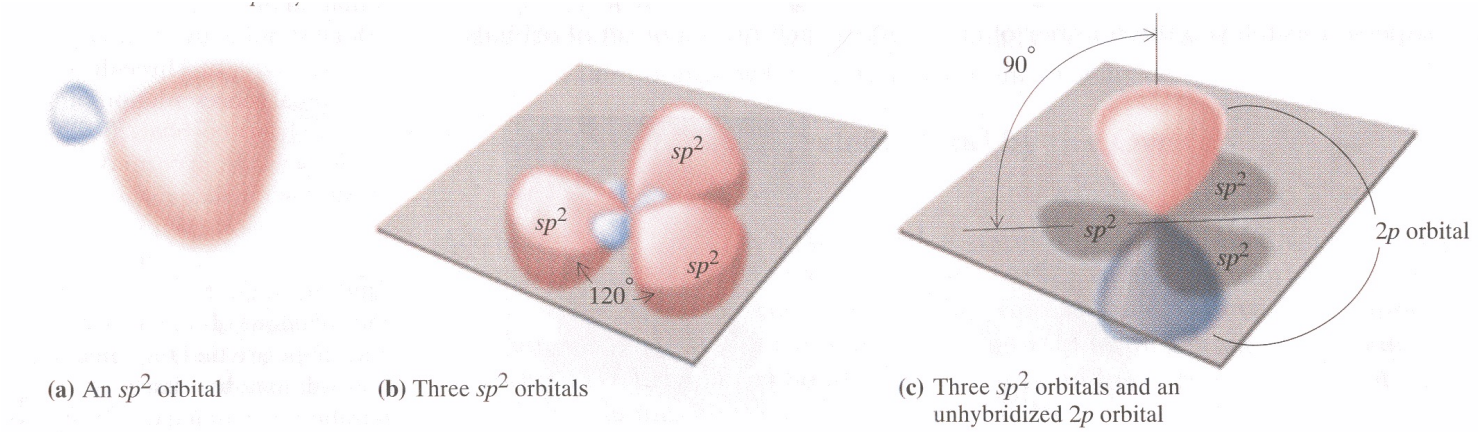


Orbitais híbridos sp^2

i) Combinação de um orbital atômico s e de dois orbitais atômicos p formam três orbitais sp^2.

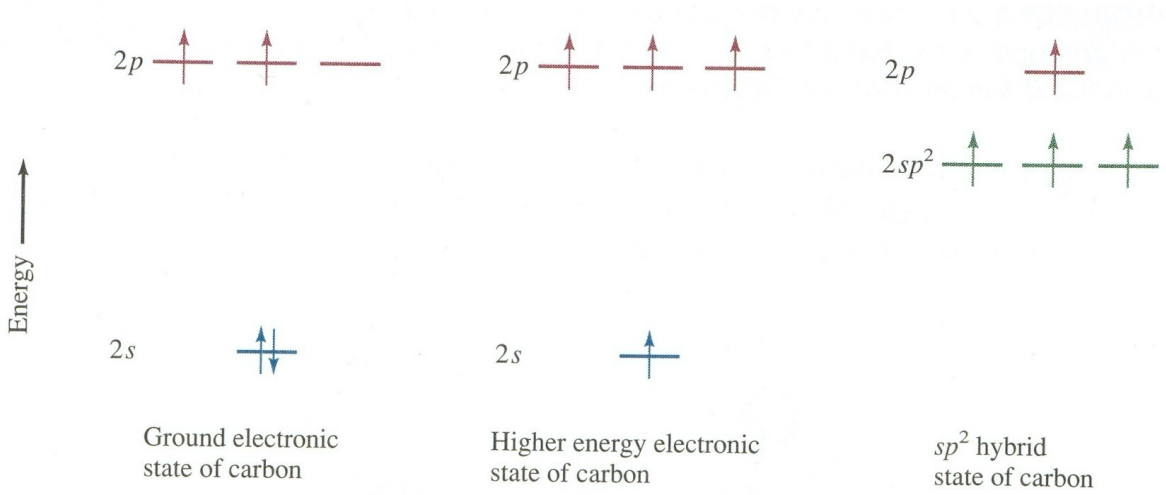
ii) Os três orbitais sp^2 têm energia equivalente.

iii) Ângulos de ligação de aproximadamente 120 °.

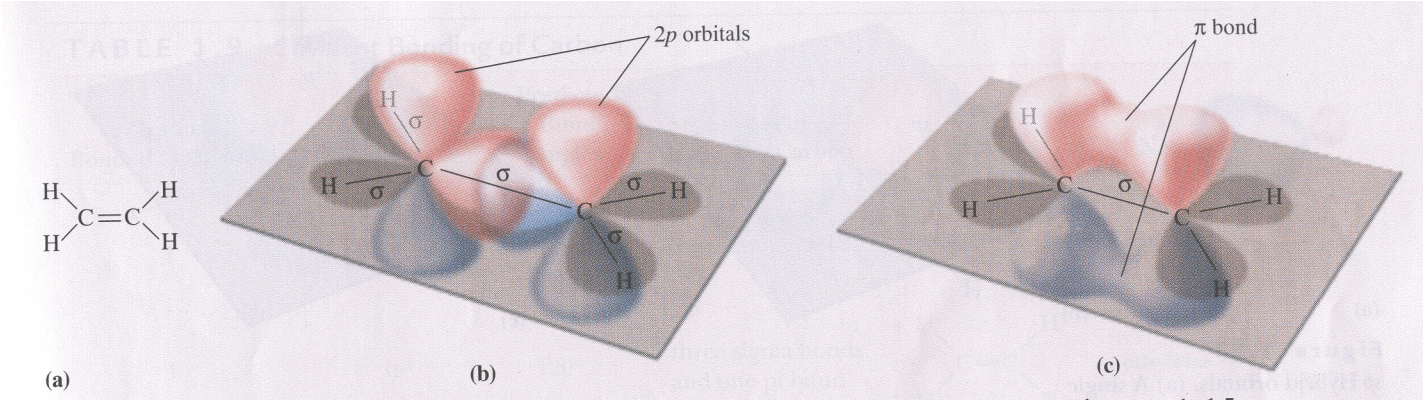


(a) An sp^2 orbital (b) Three sp^2 orbitals (c) Three sp^2 orbitals and an unhybridized $2p$ orbital

Eteno



sp^2 → formação de ligações duplas



Ligação π

a) sobreposição de orbitais paralelos $2p_z$

b) ambos os elétrons no orbital ligante (π);

orbital anti-ligante (π*) fica vazio.

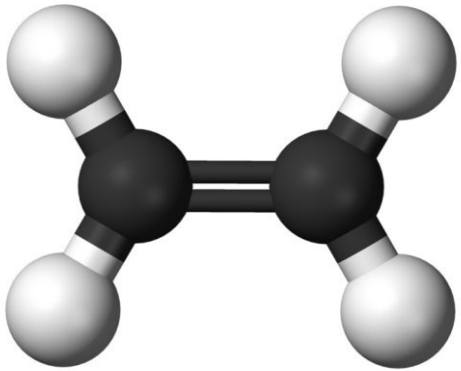
c) a rotação não é livre para uma ligação dupla.

d) seis átomos no mesmo plano,

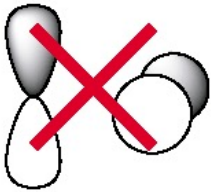
ângulos próximos a 120° .

e) duplas são menores do que as simples

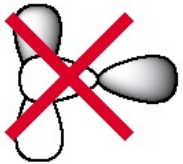
f) C-Cπ é mais fraca do que C-Cσ.



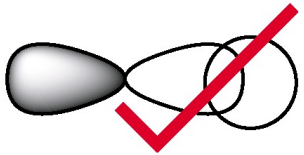
Aspectos importantes na sobreposição de orbitais



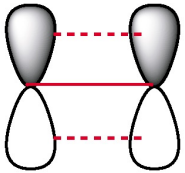
p_z and p_x



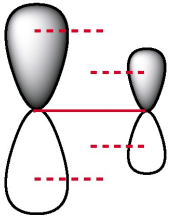
p_z and p_y



p and s
(end-on)



efficient overlap of p orbitals of the same size (same principal quantum number *n*)



inefficient overlap of p orbitals of different size (different principal quantum numbers *n*)

here the different phases of the p orbital are labelled positive and negative – this can be confusing and so is best avoided

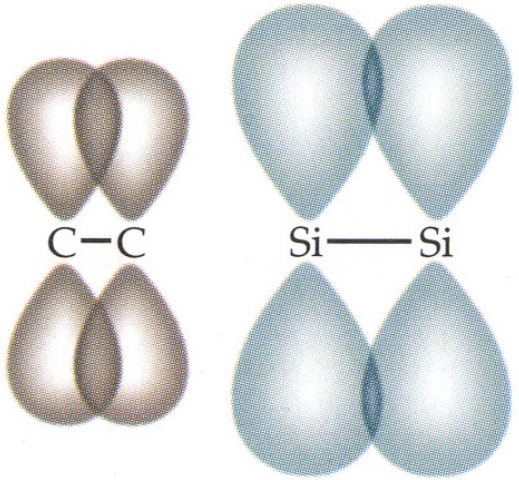
here the different phases of the p orbital are shown by shading one half and not the other

Ligação π

Ligação π: Carbono *vs* Silício

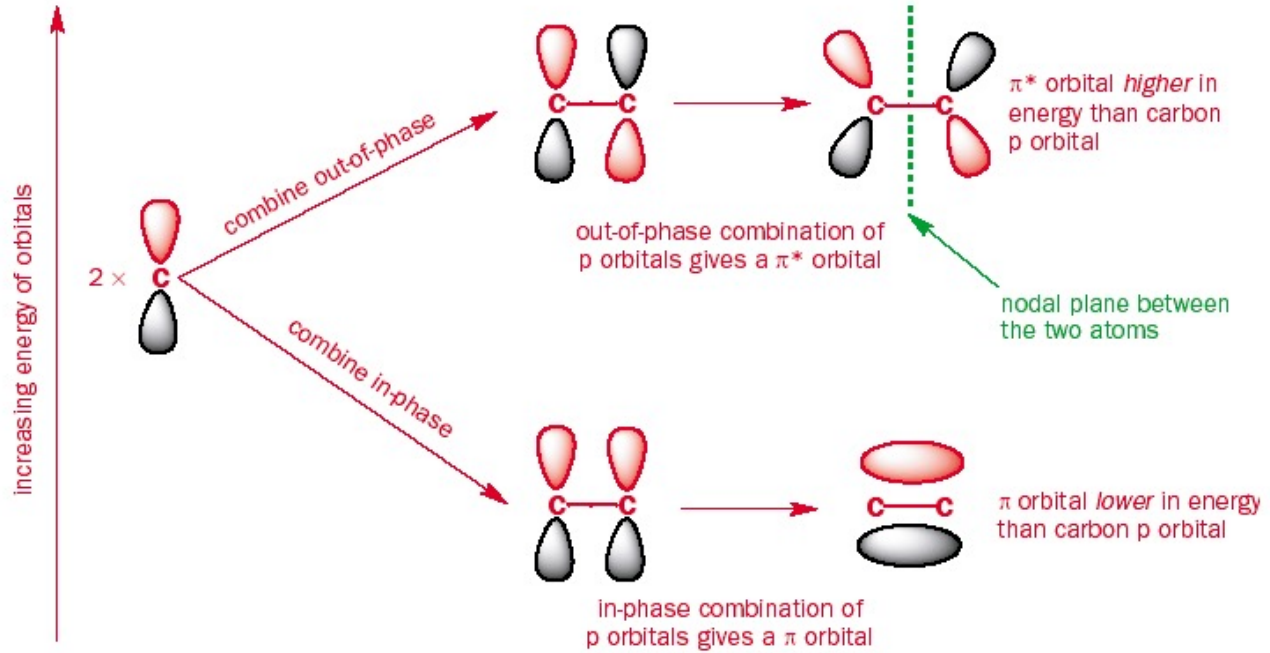
π C-C: cerca de 65 Kcal/mol

π Si-Si: cerca de 24 Kcal/mol



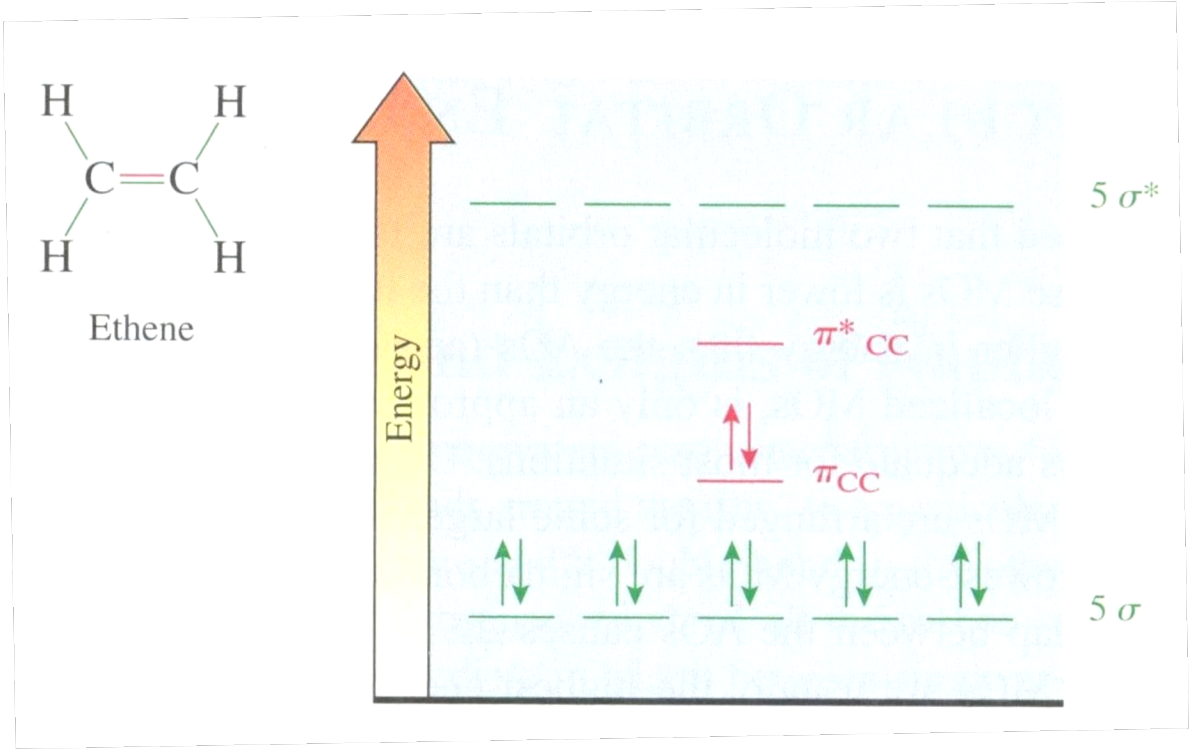
Orbitais ligante (π) e anti-ligante (π*)

(LUMO) Lowest Unoccupied Molecular Orbital



(HOMO) Highest Occupied Molecular Orbital

Eteno



Alcenos

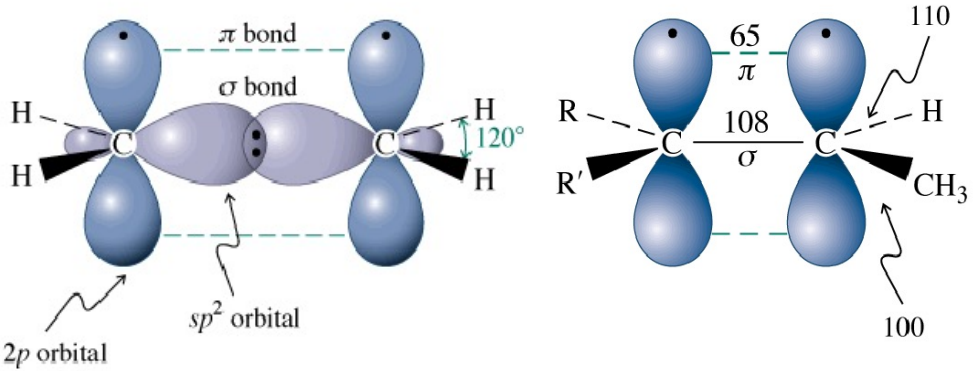
i) Planar;

ii) Dois átomos de carbono trigonal planar (sp^2);

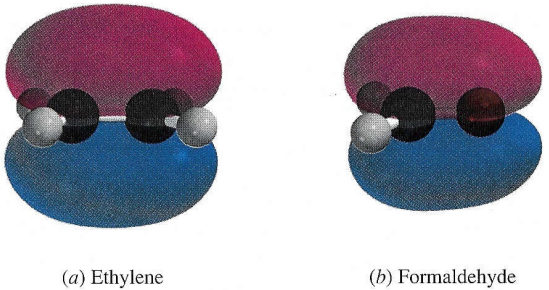
iii) Ângulos de 120º;

iv) Uma ligação σ e uma ligação π.

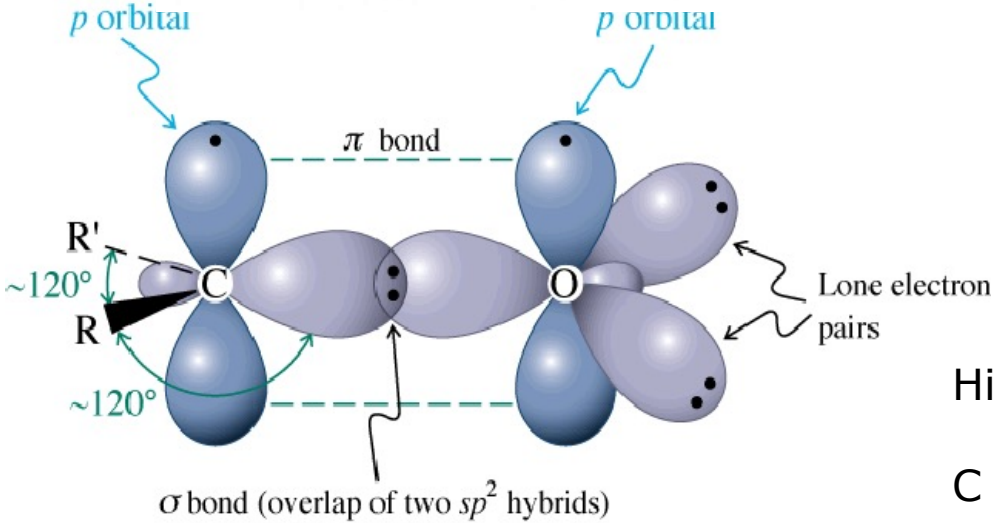
v) Ligação π não tem rotação

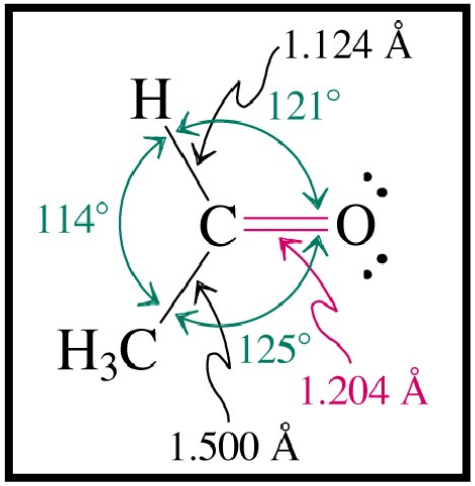


Aldeídos e cetonas



(*a*) Ethylene (*b*) Formaldehyde

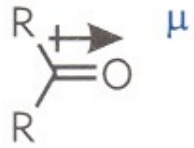




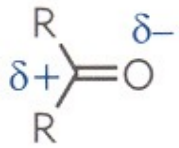
Hibridização do

C e do O é sp^2.

Aldeídos e cetonas

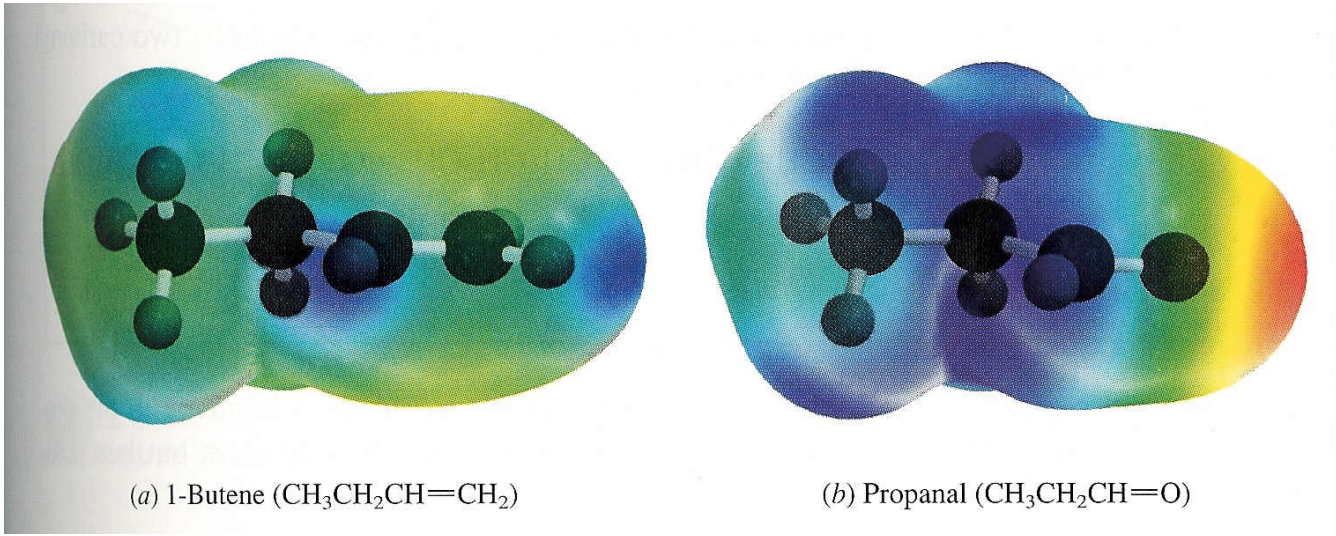


vetor momento de dipolo μ da C=O



cargas parciais na carbonila

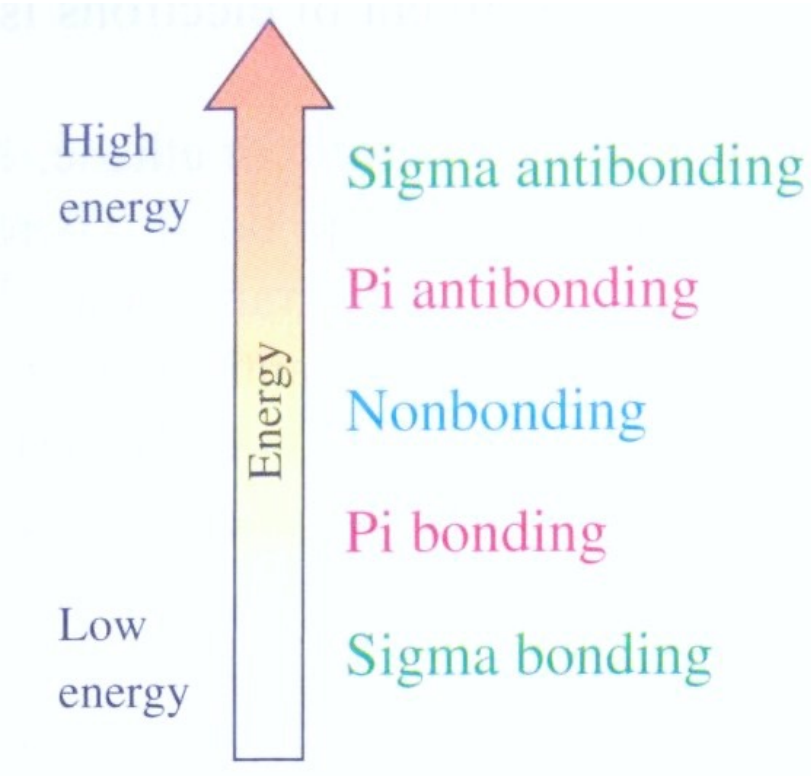
O grupo C=O é polar:
(μ = 2,2-3,0 D)



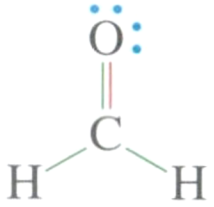
(*a*) 1-Butene ($CH_3CH_2CH{=}CH_2$)

(*b*) Propanal ($CH_3CH_2CH{=}O$)

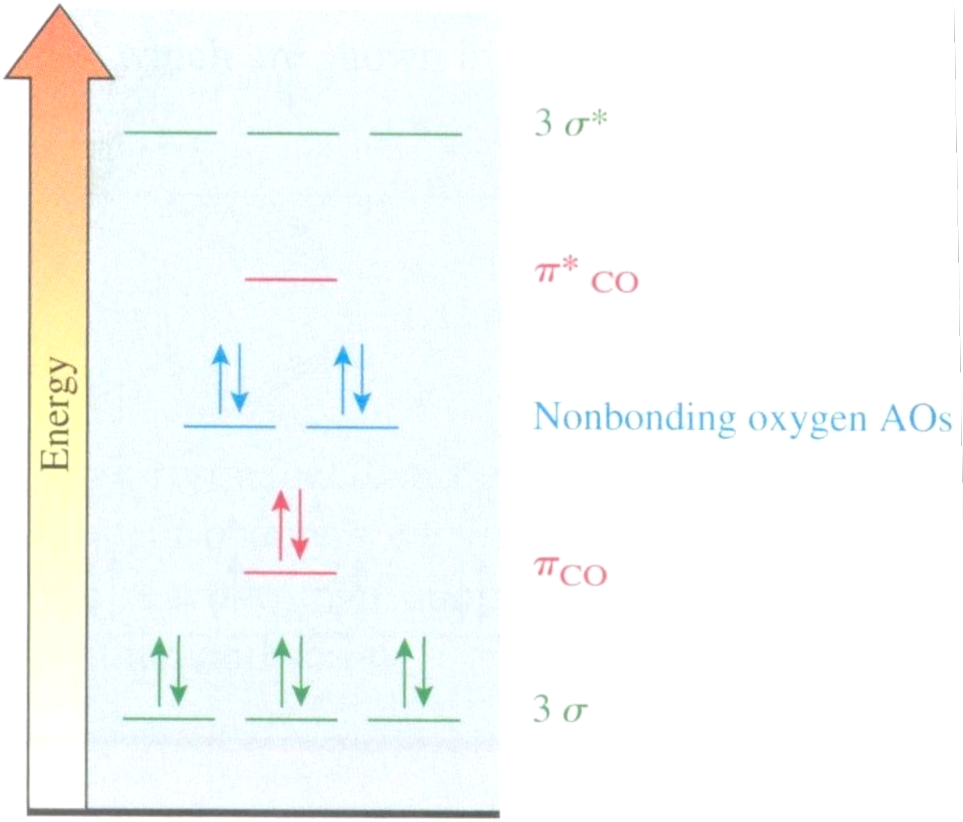
Diagrama de Energia Simplificado



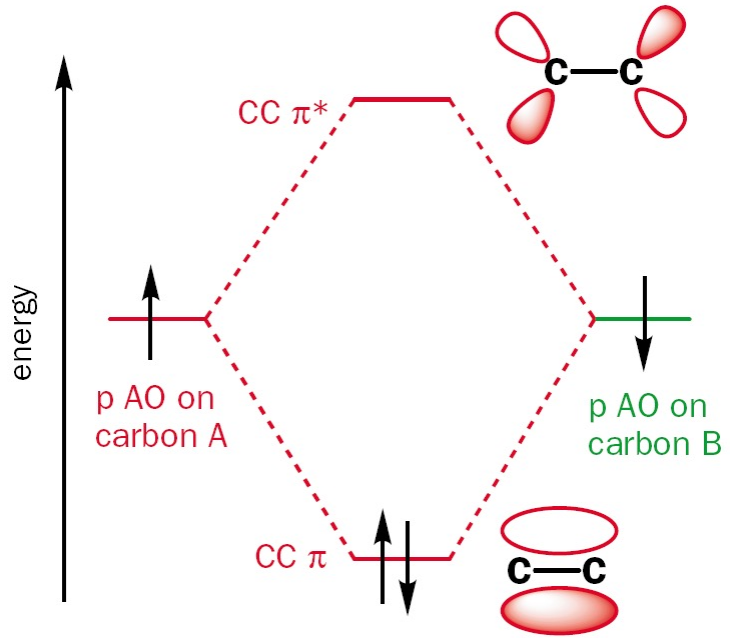
Formaldeído

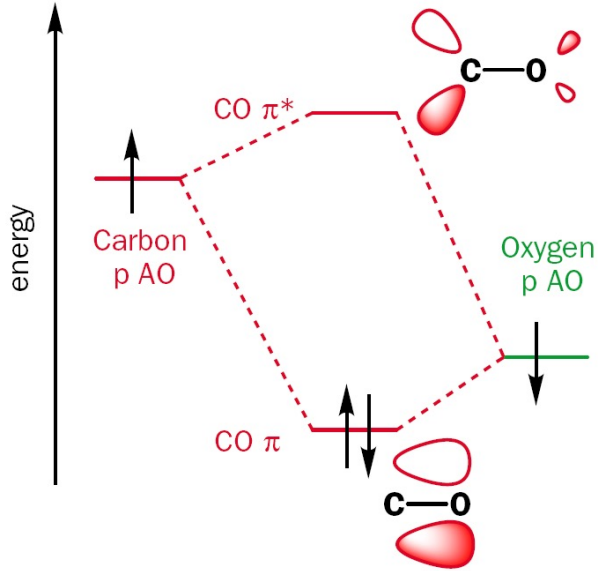


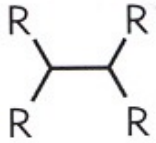
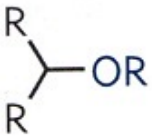
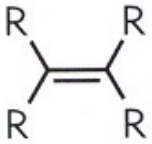
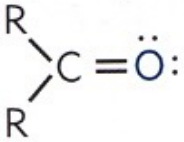
Formaldehyde



Ligação π C=O e C=C





				
comprimento de ligação (Å)	~1,54	~1,32	~1,34	~1,21
força de ligação (kcal/mol)	83-85	85-91	146-151	173-181

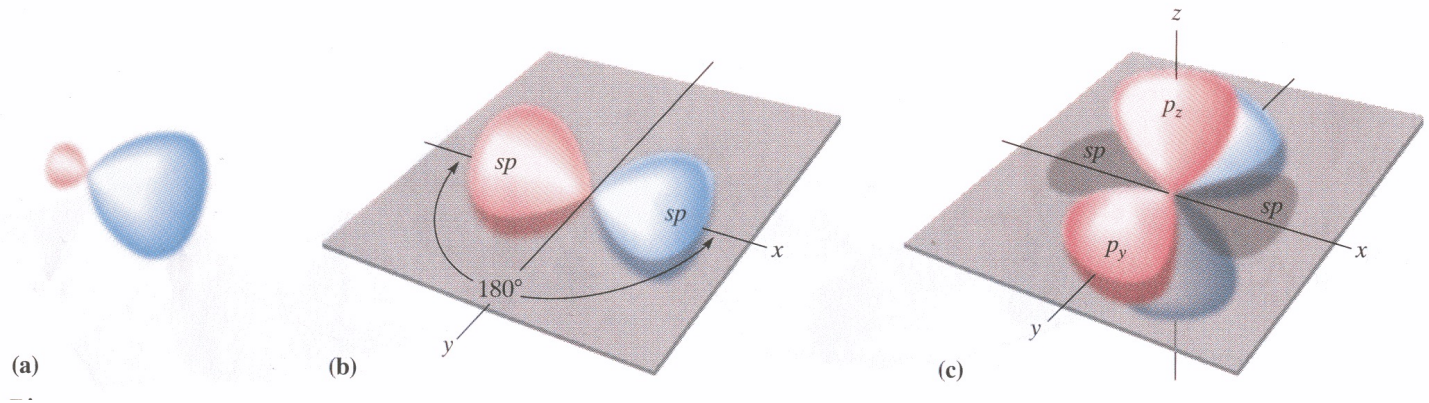
Um alto valor de energia de ligação não implica necessariamente em baixa reatividade.

Orbitais Híbridos sp

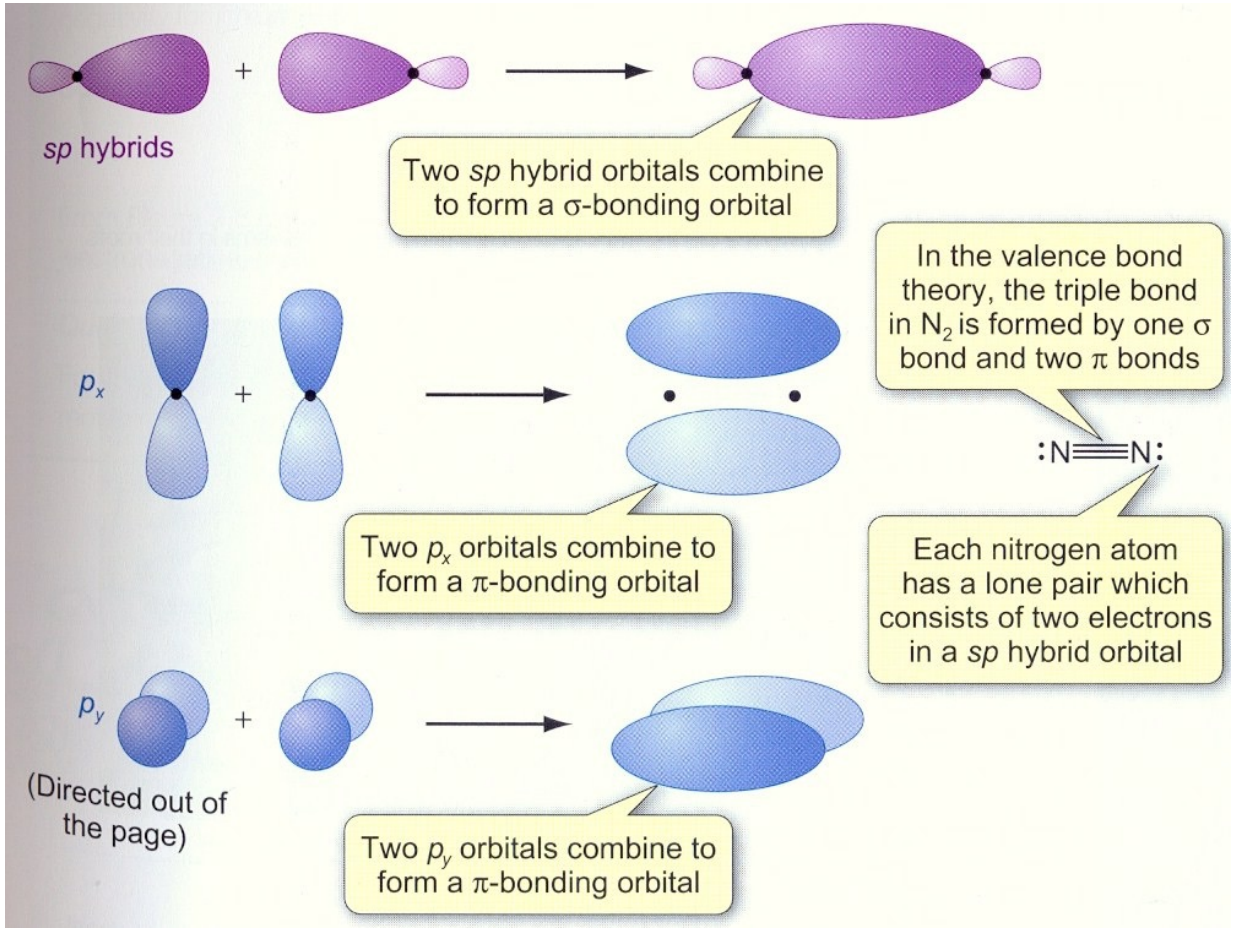
i) Combinação de um orbital atômico s e de um orbital atômico p formam dois orbitais sp;

ii) Os dois orbitais sp têm energia equivalente;

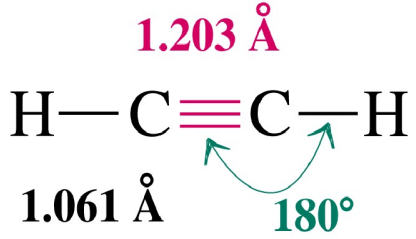
iii) ângulos de ligação de aproximadamente 180 º.



Nitrogênio


sp hybrids
Two sp hybrid orbitals combine to form a σ-bonding orbital
In the valence bond theory, the triple bond in N_2 is formed by one σ bond and two π bonds
p_x
:N≡N:
Two p_x orbitals combine to form a π-bonding orbital
Each nitrogen atom has a lone pair which consists of two electrons in a sp hybrid orbital
p_y
(Directed out of the page)
Two p_y orbitals combine to form a π-bonding orbital

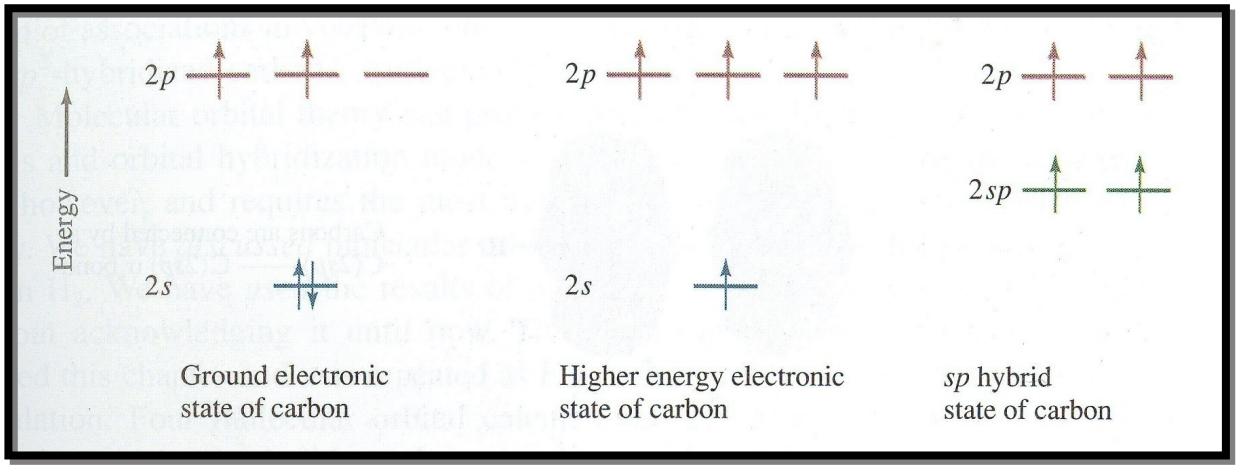
Etino



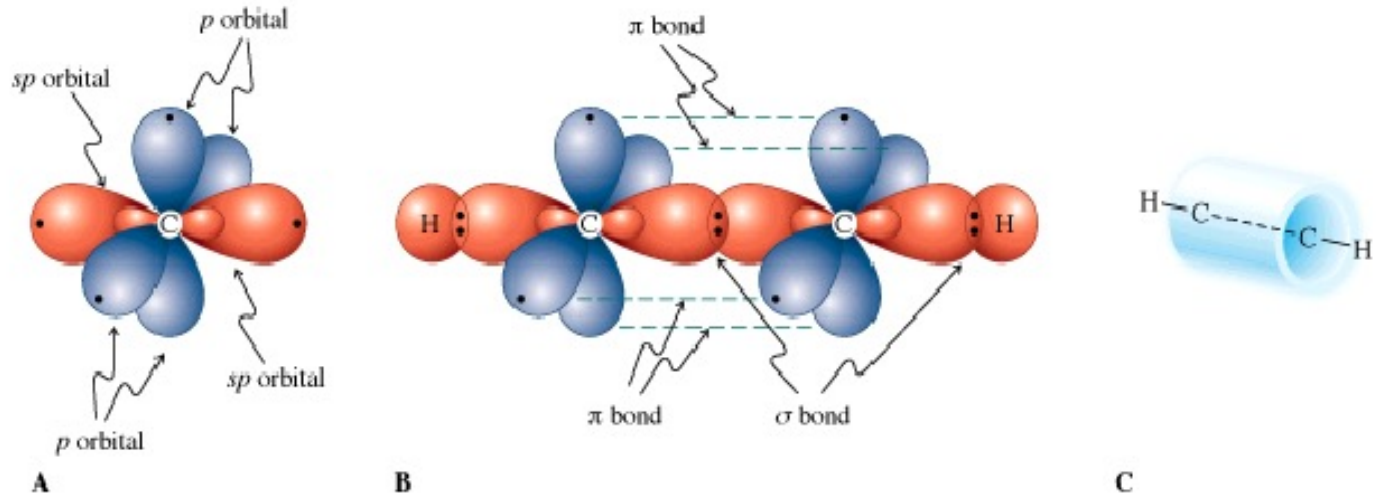
Três ligações carbono – carbono:

uma ligação σ (sp - sp)

duas ligações π (p – p)



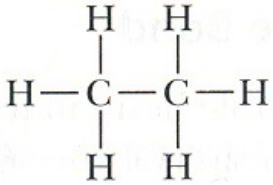
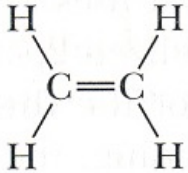
Etino



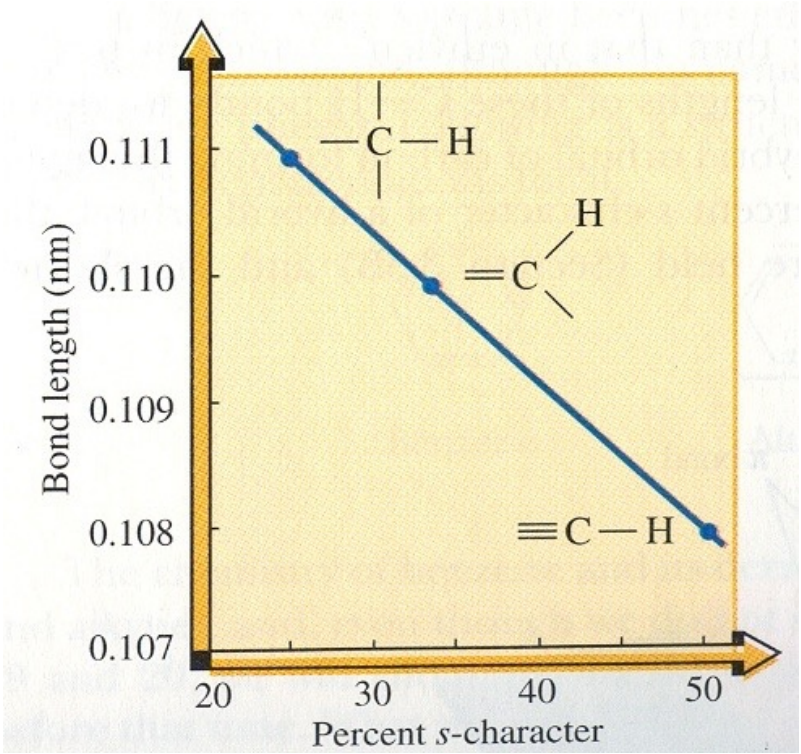
Como deve ser o Diagrama Simplificado para

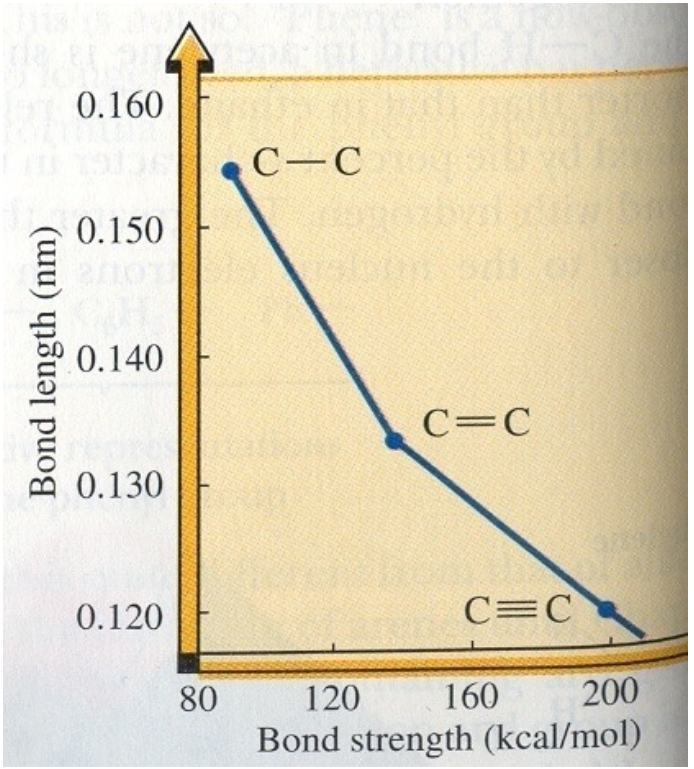
Energia dos Orbitais Moleculares do Acetileno?

Etano vs. Eteno vs. Etino

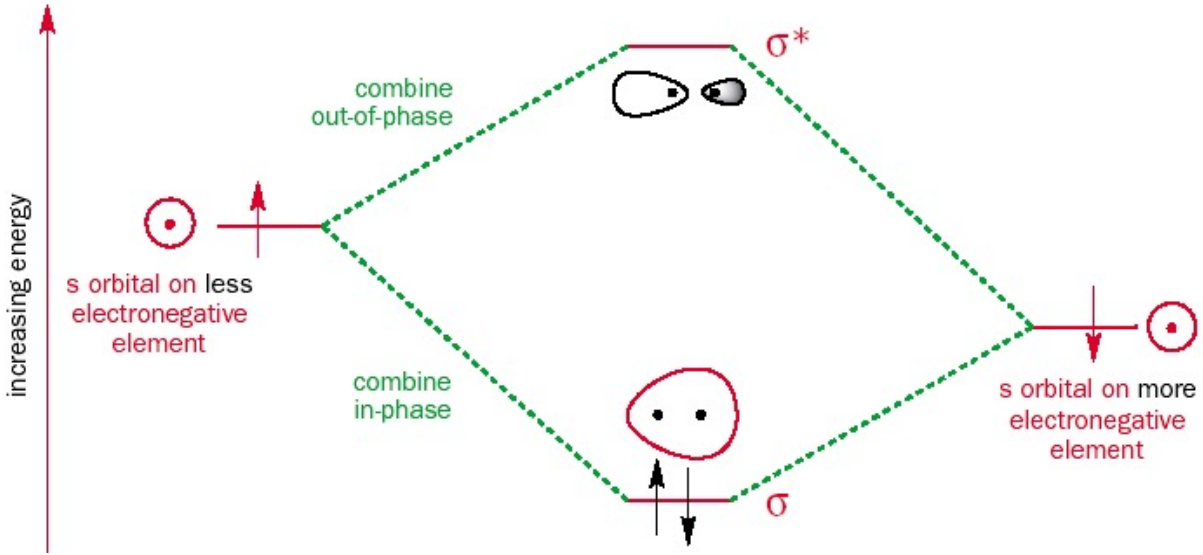
Molecule	Bond	Bond Orbital Overlap	Bond Length (Å)	Bond Strength [kcal/mol (kJ/mol)]
	C—C	sp^3-sp^3	1.54	90 (377)
	C—H	sp^3-1s	1.11	98 (410)
	C—C	sp^2-sp^2, 2p-2p	1.34	146 (611)
	C—H	sp^2-1s	1.10	104 (435)
	C—C	sp-sp, two 2p-2p	1.21	200 (837)
	C—H	sp-1s	1.08	125 (523)

Etano vs. Eteno vs. Etino





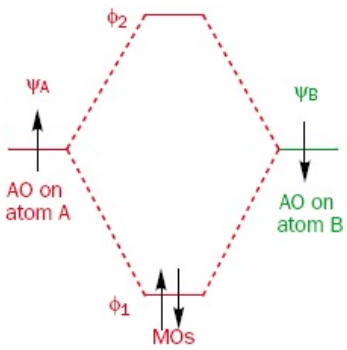
Ligações entre átomos distintos



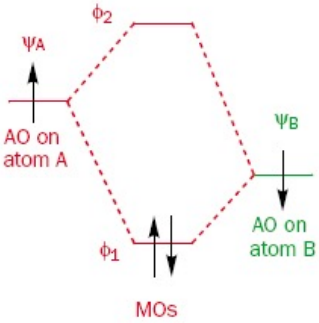
Quanto mais eletronegativo for um átomo, mais baixos serão os OAs e, assim, quaisquer elétrons neles serão mantidos com mais força.

Ligações polares

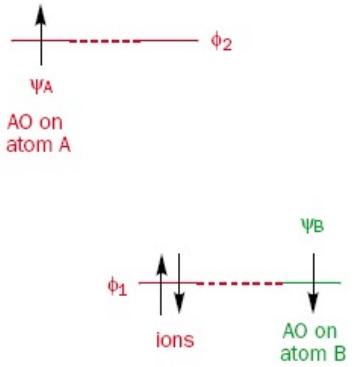
Energies of AOs both the same



AO on atom B is a *little* lower in energy than AO on atom A



AO on atom B is a *lot* lower in energy than AO on atom A



Classificação das ligações químicas

Diferença de Eletronegatividade Entre os Átomos Ligados	Tipo de Ligação
menor do 0,5	covalente não polar
0,5 a 1,9	covalente polar
maior do que 1,9	iônica

Em ligações covalentes polares: *átomo mais eletronegativo: δ^-*

átomos menos eletronegativo: δ^+

Exemplo:

ligação C–O: 3,5 – 2,5 = 1,0 δ^+ δ^-

covalente polar C–O

Valores de Eletronegatividade de Pauling