Bonding in organic molecules

Dissociation energies os some bonds [kJ/mol]

C-H	413	C-C	346	C=C	610	C≡C	837
C-N	309	C=N	615	C≡N	887	C-S	272
C-Cl	339	C-Br	284	C-I	213	N-N	163
O-O	166	O=O	498	S-S	226	F-F	153
I-I	151	H-O	463	H-N	391	H-S	347
H-Br	366	H-I	299	O-Cl	217	O-Br	201
C-O	357	C=O	737	C=S	535	C-F	444
N=N	418	N≡N	941	Br-Br	193	Cl-Cl	243
H-F	570	H-Cl	431				

Dissociation energies of C-H bonds in connection with the structure of hydrocarbon skeleton [kJ/mol]

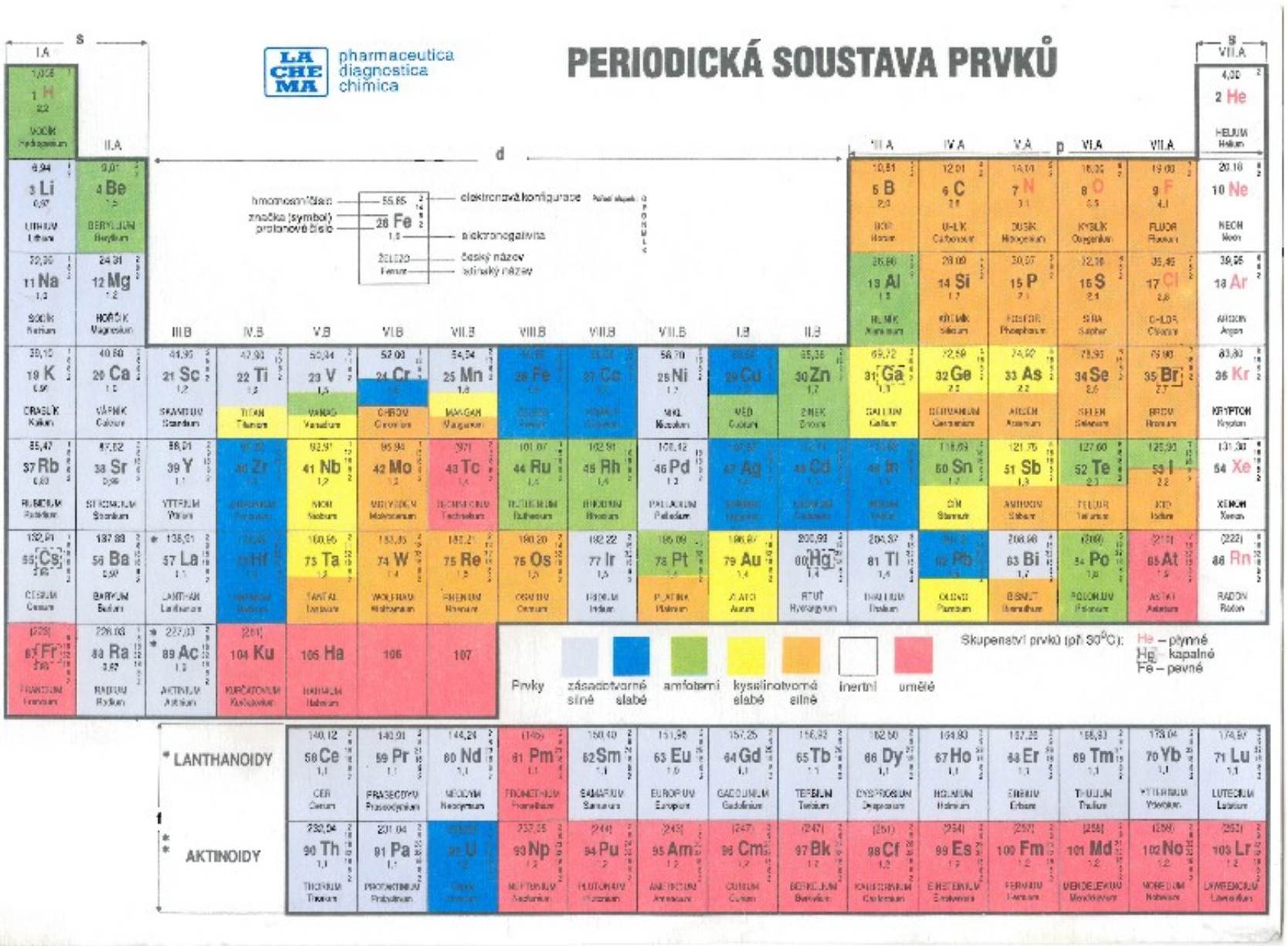
CH_3-H	427	CH_3 \ CH-H / CH_3	393	C_6H_5-H	427
C_2H_5-H	405			C_6H_5-CH_2-H	326
n-C_3H_7-H	405	$(CH_3)_3$C-H	381	CH_2=CH-H	435

Bonding in organic molecules

Average bond length in organic molecules [nm]

C-C	0,154	C=C	0,134	C≡C	0,120
C-H	0,111	C-O	0,141	C=O	0,120
C-N	0,147	C=N	0,128	C≡N	0,116
C-S	0,181	C=S	0,156	C-F	0,138
C-Cl	0,178	C-Br	0,194	C-I	0,214

Bonding in organic molecules



Bonding in organic molecules

Electronegativity of chosen elements by Pauling

H 2,20						
	Li 0,98	Be 1,57	B 2,04	C 2,55	N 3,04	O 3,44	F 4,00
	Na 0,93	Mg 1,31	Al 1,51	Si 1,90	P 2,19	S 2,58	Cl 3,16
					As 2,18	Se 2,55	Br 2,96
							I 2,66

Bonding in organic molecules

Elements electronegativity	
C	2,55
H	2,20
O	3,44
N	3,04
Cl	3,16
Br	2,96
I	2,66
S	2,58

DIPOLE MOMENT

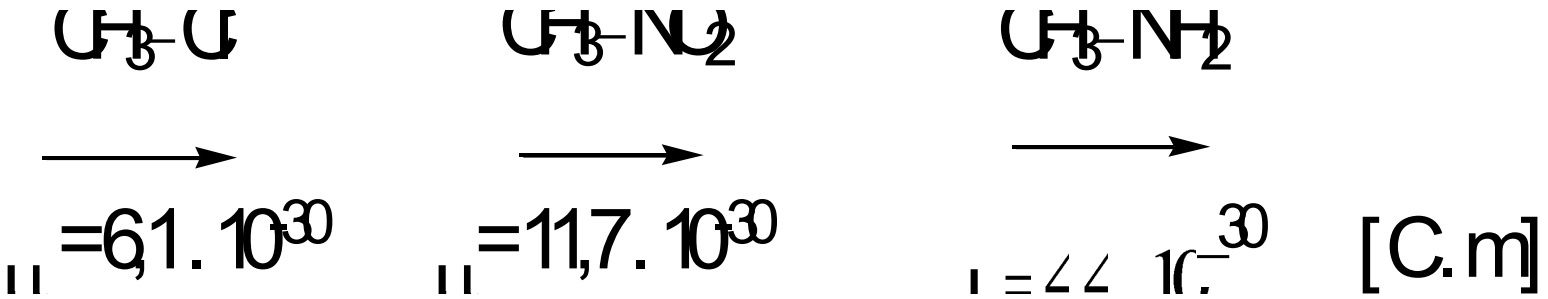
$\mu = e \cdot d$

e atom charge [C]

d distance [m]

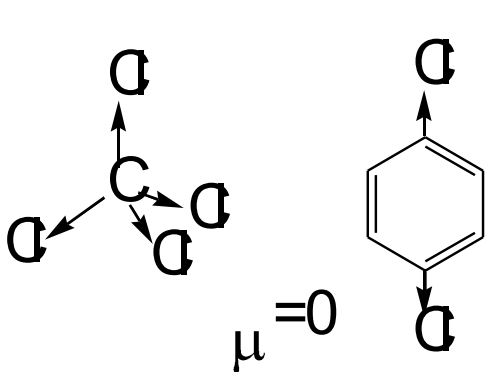
Dipole moment is a vector – with value and direction

	μ		μ
H - C	1,33	C – N	0,73
H - N	4,36	C – O	2,46
H - O	5,03	C = O	7,65
		C ≡ N	11,65

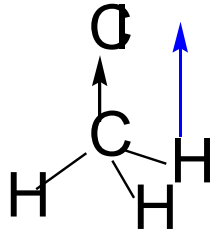


Bonding in organic molecules

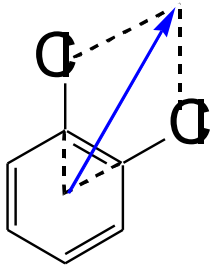
Dipole moment - vector



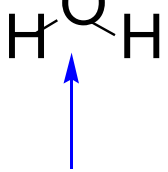
$\mu = 0$



$\mu = 6{,}23 \cdot 10^{-30}\ C.m$



$\mu = 7{,}5 \cdot 10^{-30}\ C.m$



$\mu = 6{,}16 \cdot 10^{-30}\ C.m$

Most of reactions is realized in a solvent , that by the solvation can influence the charge distribution in the molecule

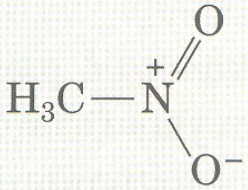
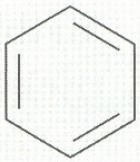
In the older literature you can find expression of dipole moment in units **D**

1D = 3,33564 . 10^{-30} C . m

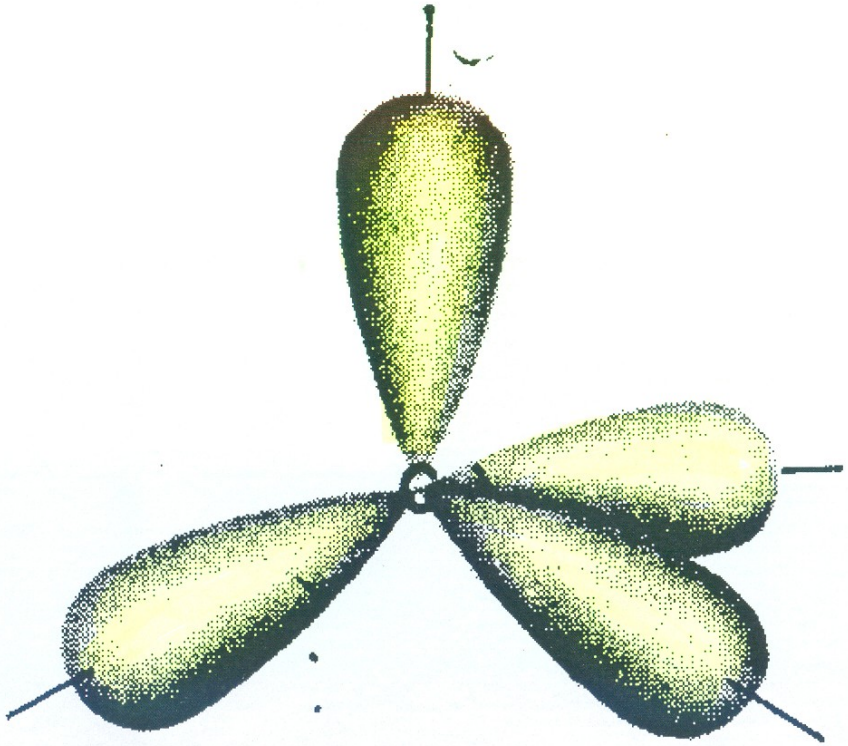
Bonding in organic molecules

Dipole moment - vector

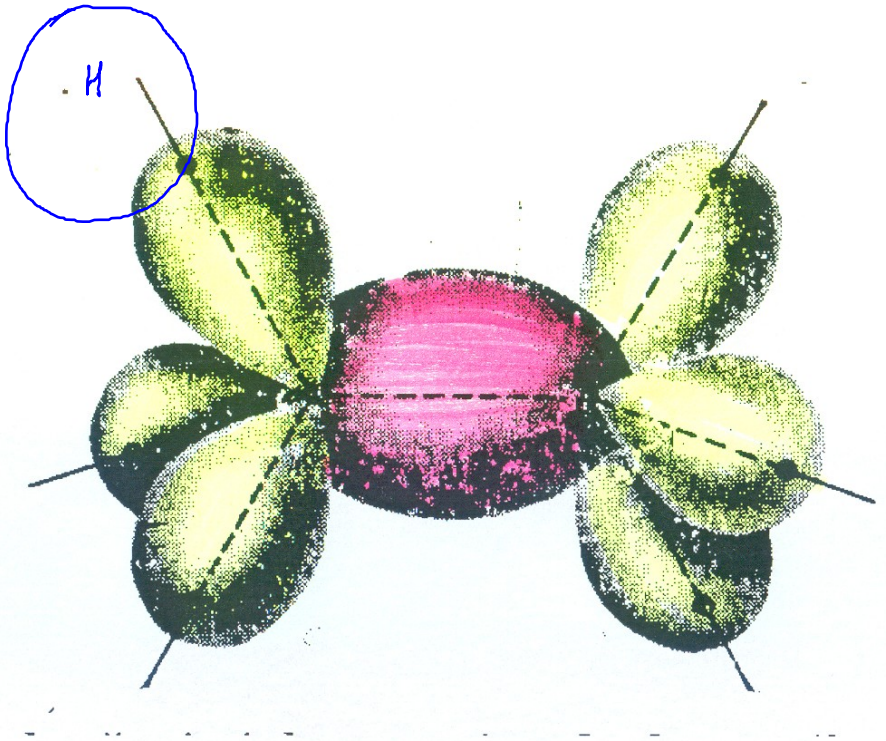
Dipole moments of some molecules

Compound	Dipole moment 10^{30} C m	Dipole moment D	Compound	Dipole moment 10^{30} C m	Dipole moment D
NaCl	30,02	9,0	NH_3	4,90	1,47
 nitromethan	11,54	3,46	CH_4	0	0
			CCl_4	0	0
			CH_3CH_3	0	0
CH_3Cl	6,24	1,87	 benzen	0	0
H_2O	6,17	1,85			
CH_3OH	5,67	1,70			
 diazomethan	5,00	1,50	BF_3	0	0

Bonding in organic molecules



Carbon atom in sp^3 state



Bond C-C by overlap of sp^3 orbitals

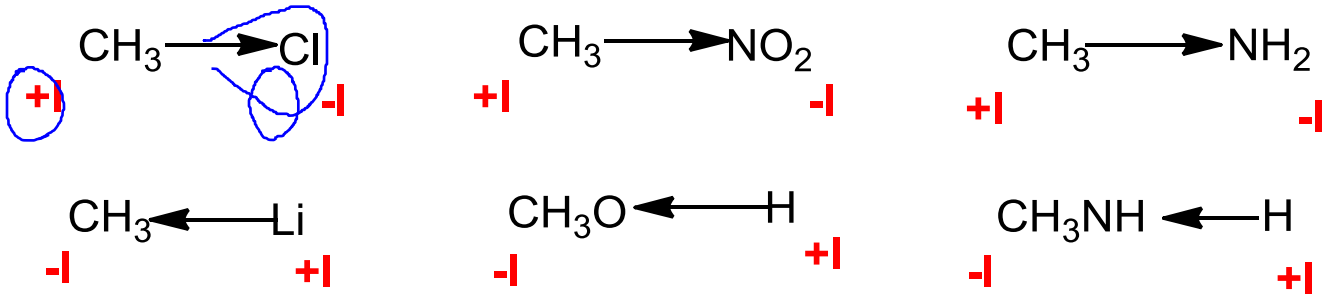
Bonding in organic molecules

Elektronegativity of elements	
C	2,55
H	2,20
O	3,44
N	3,04
Cl	3,16
Br	2,96
I	2,66
S	2,58

Bond polarity Inductive effekt

Based upon different electronegativity of bonded atoms, the electrons in bonds are shifted more or less in the bond towards one of the atoms.

The shift in single bonds (σ–bonds) is called **inductive effect**



Inductive effects of some atoms and groups

- I effect

$-F > -OR > -NH_2$
$-C{\equiv}CR > -CR{=}CR_2$
$-{}^{+}OR_2 > -{}^{+}NR_3$

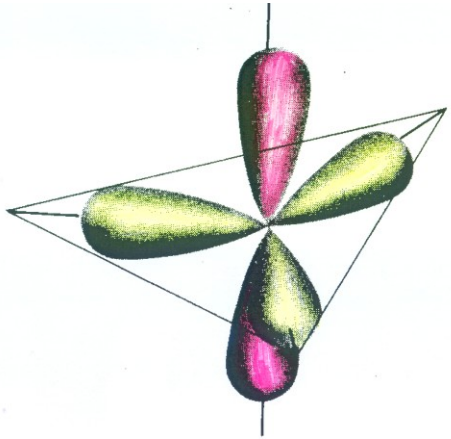
$-F > -Cl > -Br > -I$
$-NO_2 > -NO$
$-{}^{+}OR_2 > -{}^{+}SR_2$

$-OR > -SR$
$-{}^{+}OR_2 > -OR$

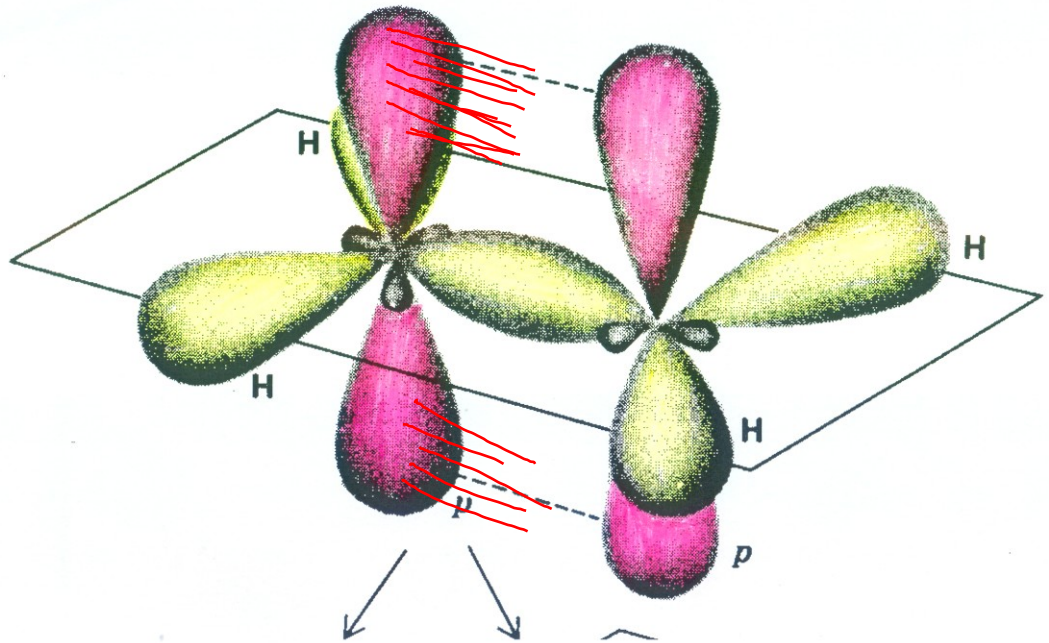
+ I effect

$-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3 > -CH_3$
$-O^{-} > -S^{-}$
$-NR^{-} > -O^{-}$

Bonding in organic molecules



C atom in sp^2 hybrid state

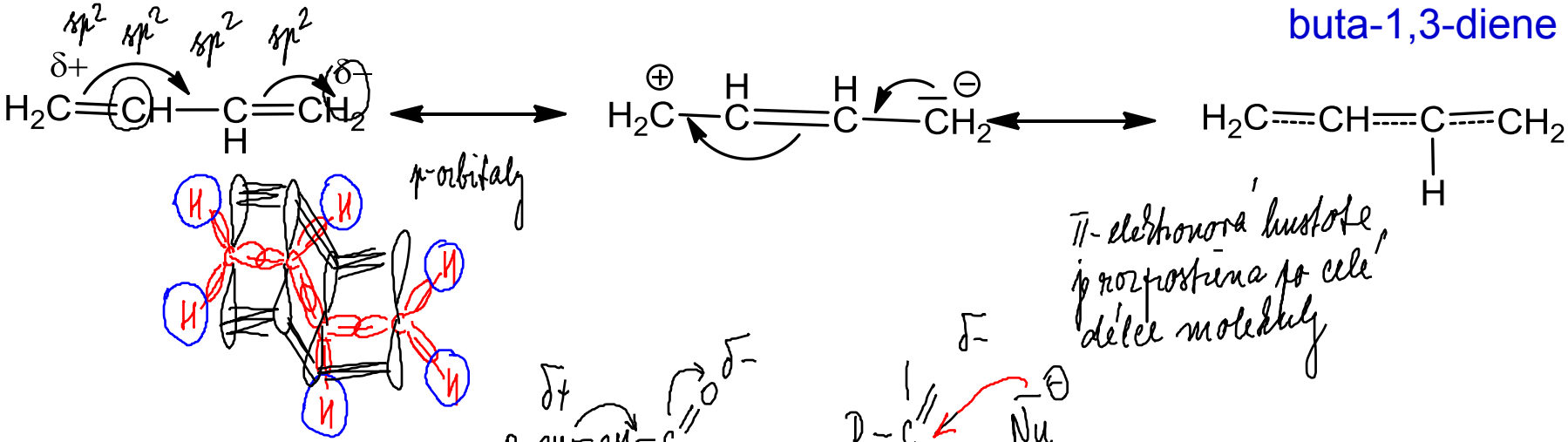


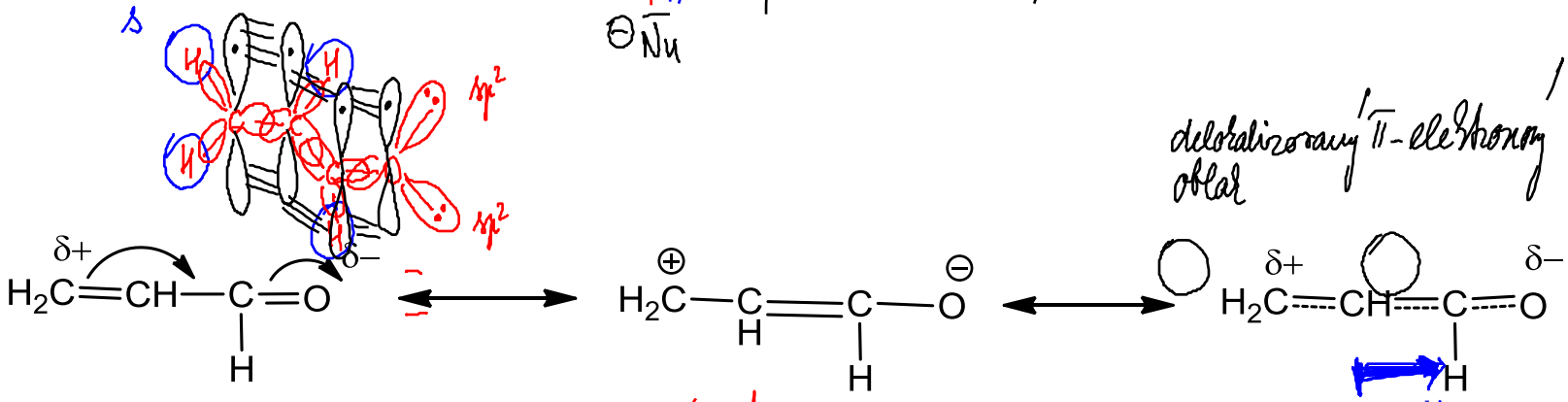
Formation of π bond between carbon atoms in sp^2 hybrid state

Bonding in organic molecules

Molecules with conjugation – mesomeric (conjugation effect) + M , - M

buta-1,3-diene





A ⇌ B rovnovážná reakce

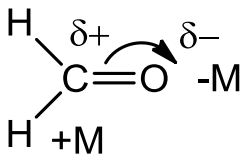
propenal

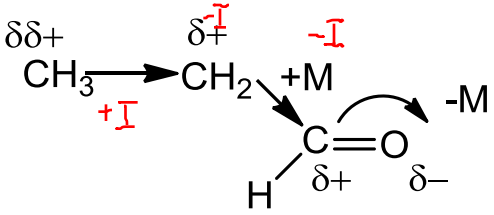
$\mu = 12{,}2 \cdot 10^{-30}$ C . m

Bonding in organic molecules

MESOMERIC (CONJUGATION) EFFECT

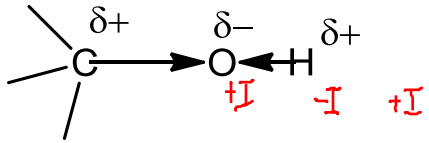
Mesomeric effect you can meet at multiple bonds (π – bonds)



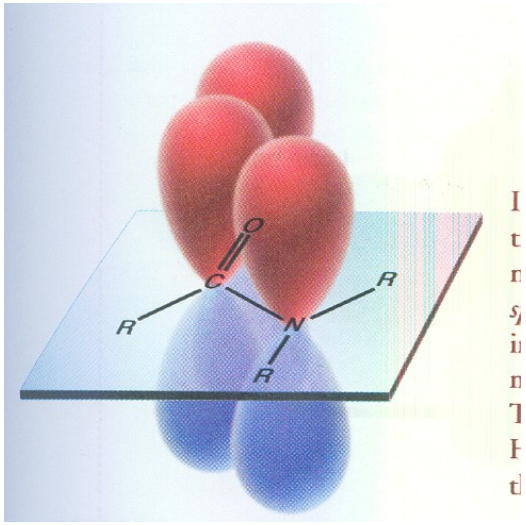


$\mu = 7{,}6 \cdot 10^{-30}$ C . m

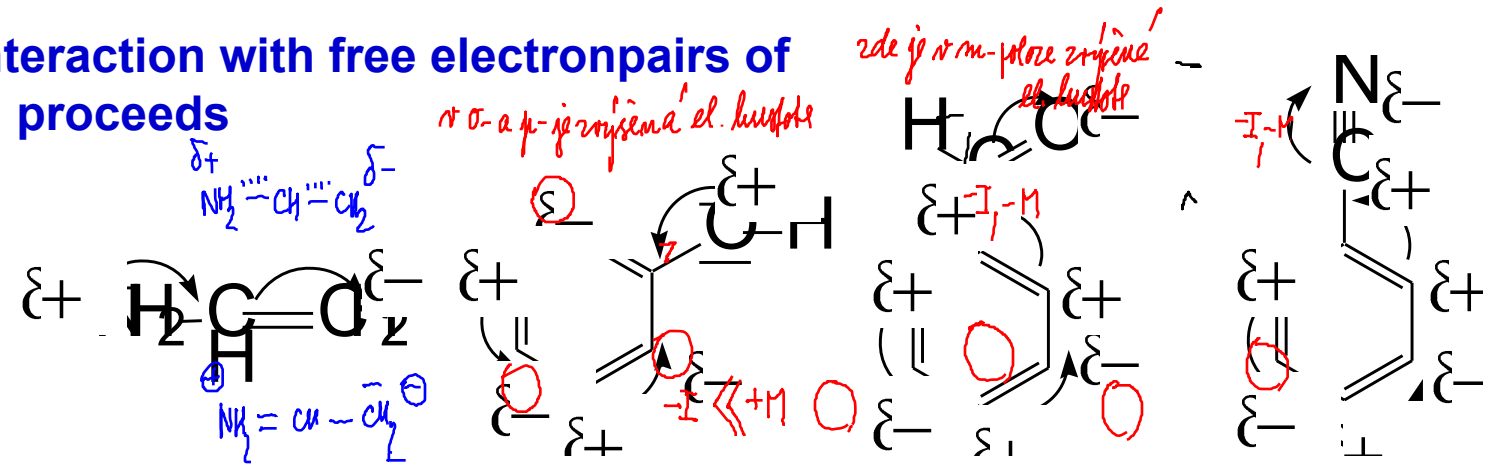
$\mu = 9{,}0 \cdot 10^{-30}$ C . m



$\mu = 2{,}46 \cdot 10^{-30}$



Very often interaction with free electronpairs of heteroatoms proceeds



Bonding in organic molecules

Rules for working with resonance structures

Particular resonance structures are not real structures, they are imaginary only. The real structure consists from different structures they are trying to depict the real structure ; real structure is an resonance hybrid. Compounds like nitromethane, benzene or acetate anion have only one structure, which is not oscilating among the resonace structures. But way of their presentation at a paper may differ.

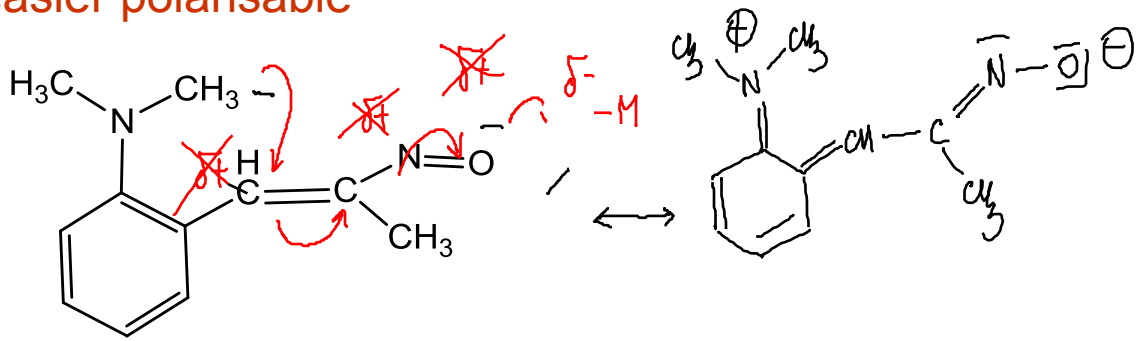
Resonance structures are differing by position of π- and non-bonding electrons only. When going from one resonance structure to another neither position nor hybridization of any of the atoms is changed. Thus, nitromethane has nitrogen atom in sp^2 hybridization and oxygen atoms keep in both resonance structures their position. They differ by position of π-electrons in N=O bond and by position of free electron pairs at oxygen atom. The electrons transfer when coming from one resonance structure to another is depicted by arrows. An arrow is always only showing transfer of electrons; no transfer of atoms. The point of arrow remembers that electron pairs are only formaly transfered from an atom or a bond towards to an atom or a bond in the point of arrow.

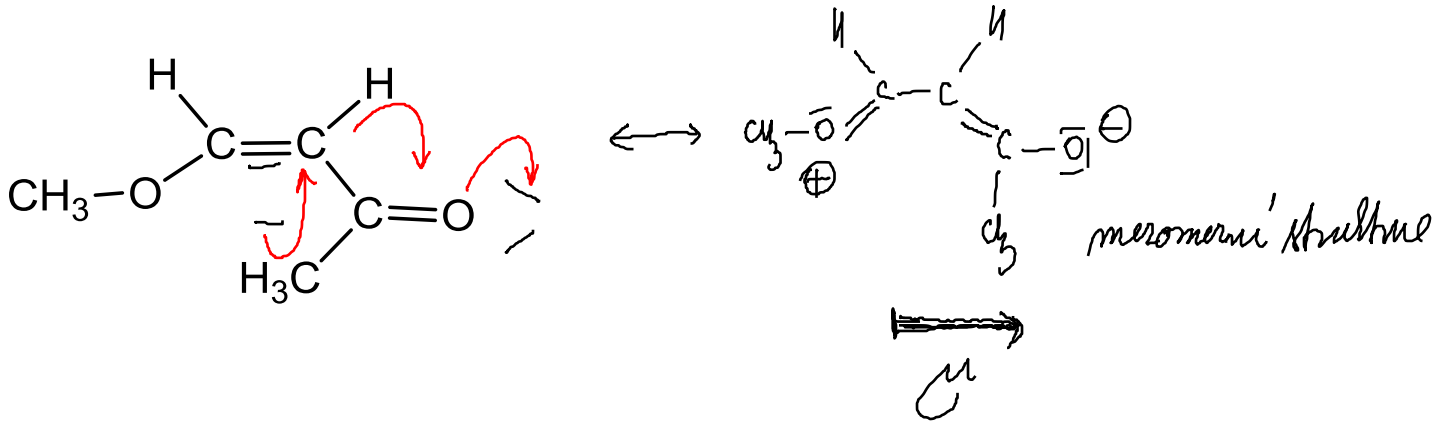
Bonding in organic molecules

When evaluate electron distribution in molecule , we are faced often to **simultaneous inductive and mesomeric effekt.**

When the action is directed in the same direction, there is no problem.

In the case the effects have different direction, **mesomeric effect is the prevailing** - (effect at multiple bonds), because π electrones are more mobile – easier polarisable





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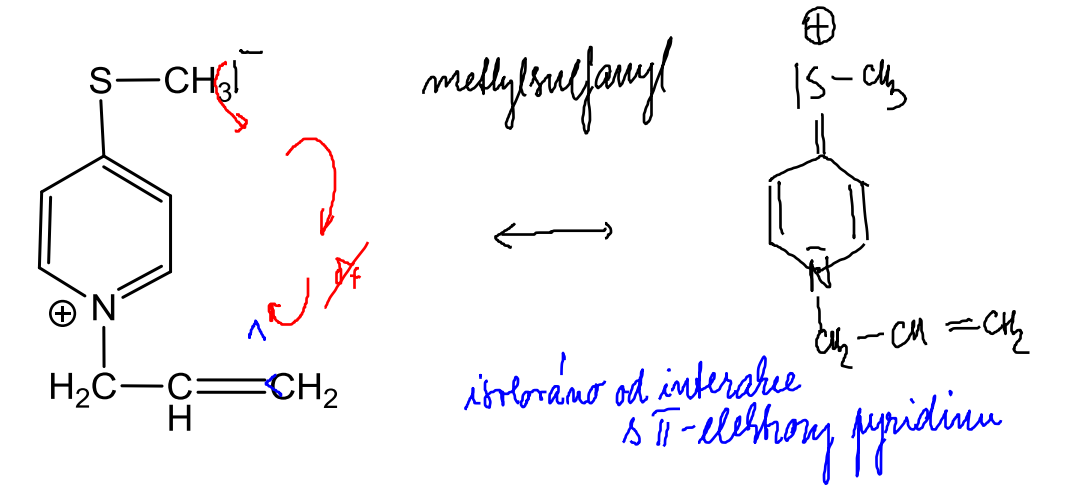
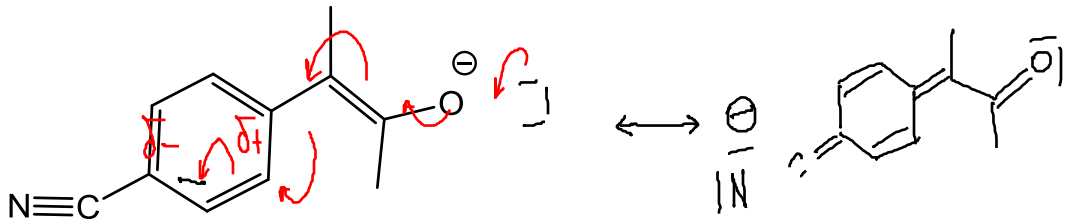
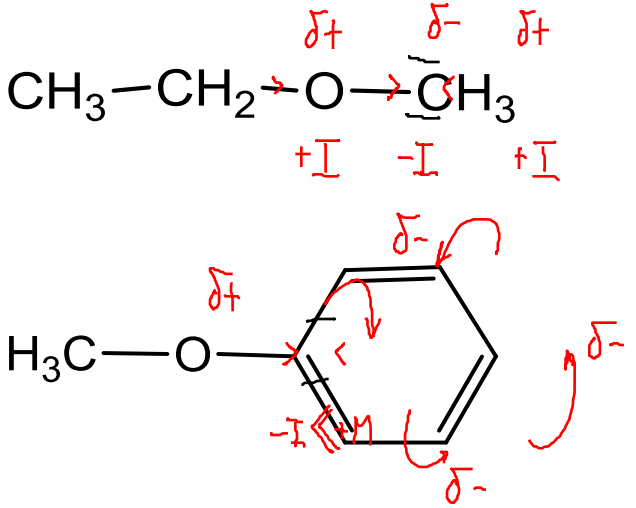


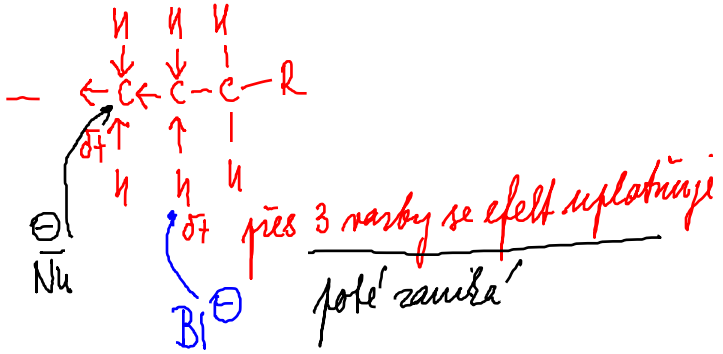


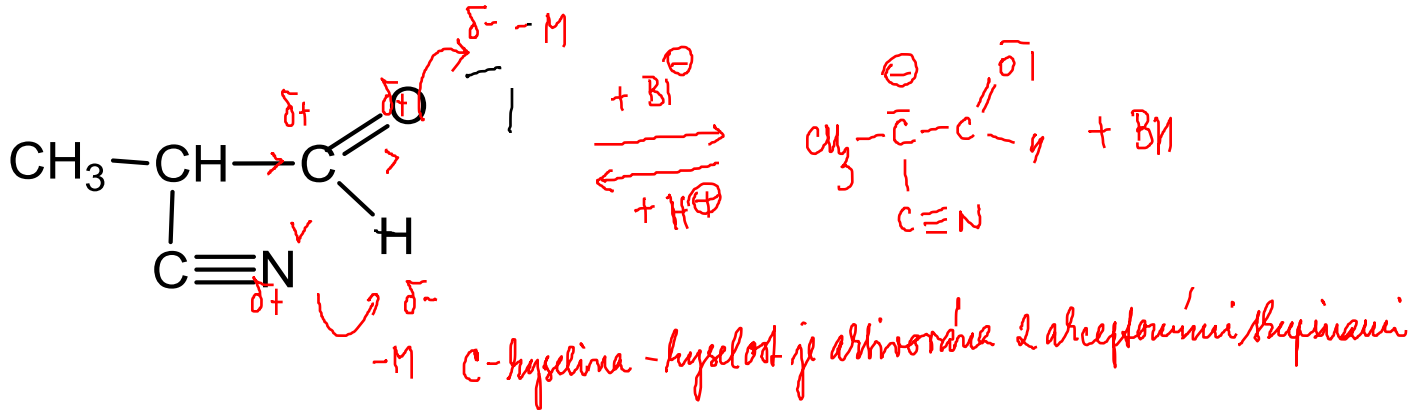
Bonding in organic molecules

!!Attention!!

The same group can behave different way at aliphatic and aromatic ring!!







Bonding in organic molecules

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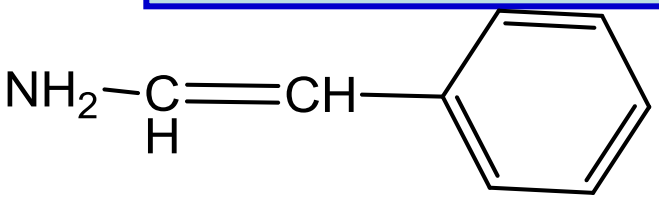

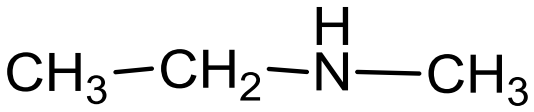

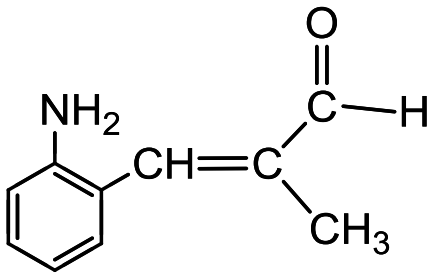

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