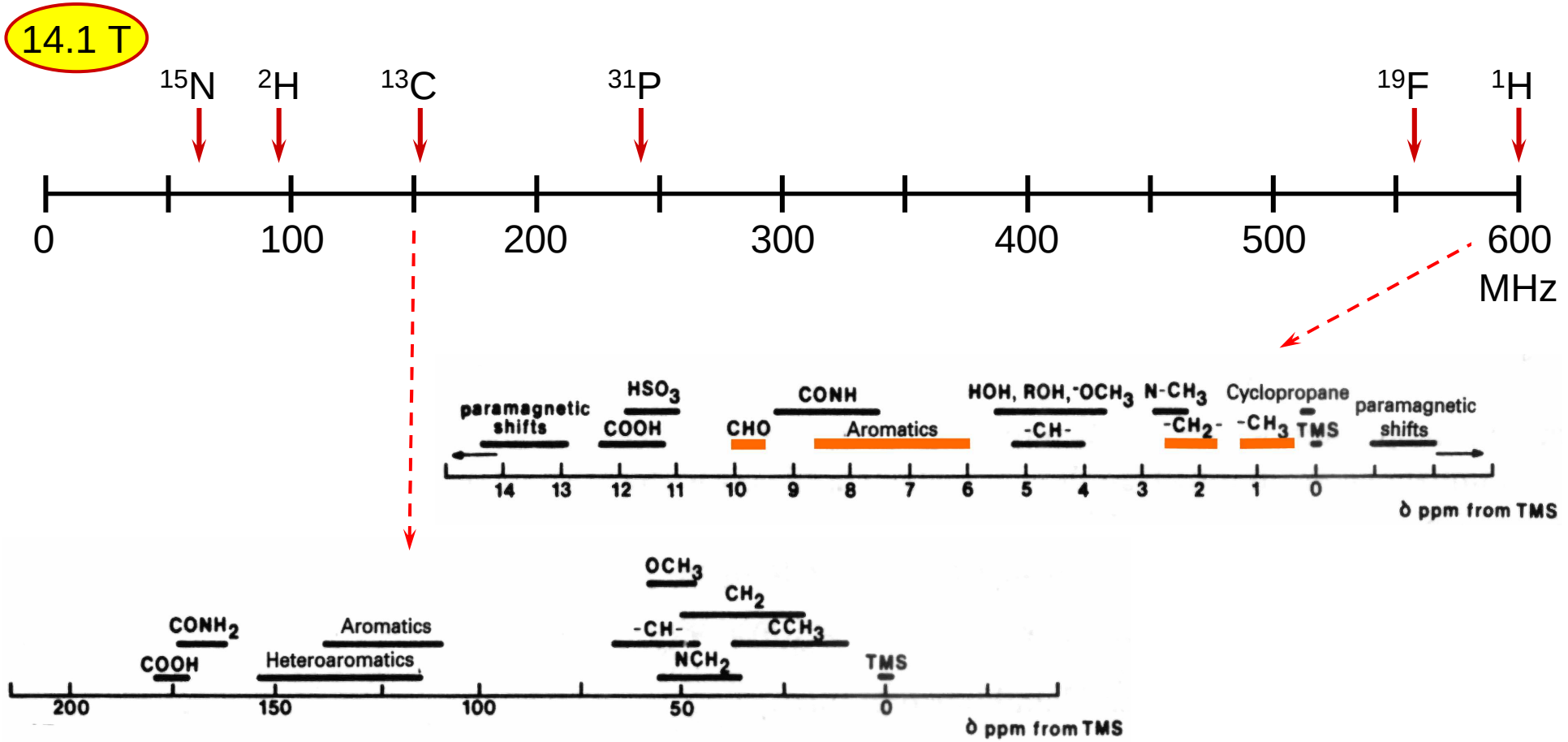
^{1}H NMR spektroskopie

Chemické posuny, J interakce

Které spektrum měříme

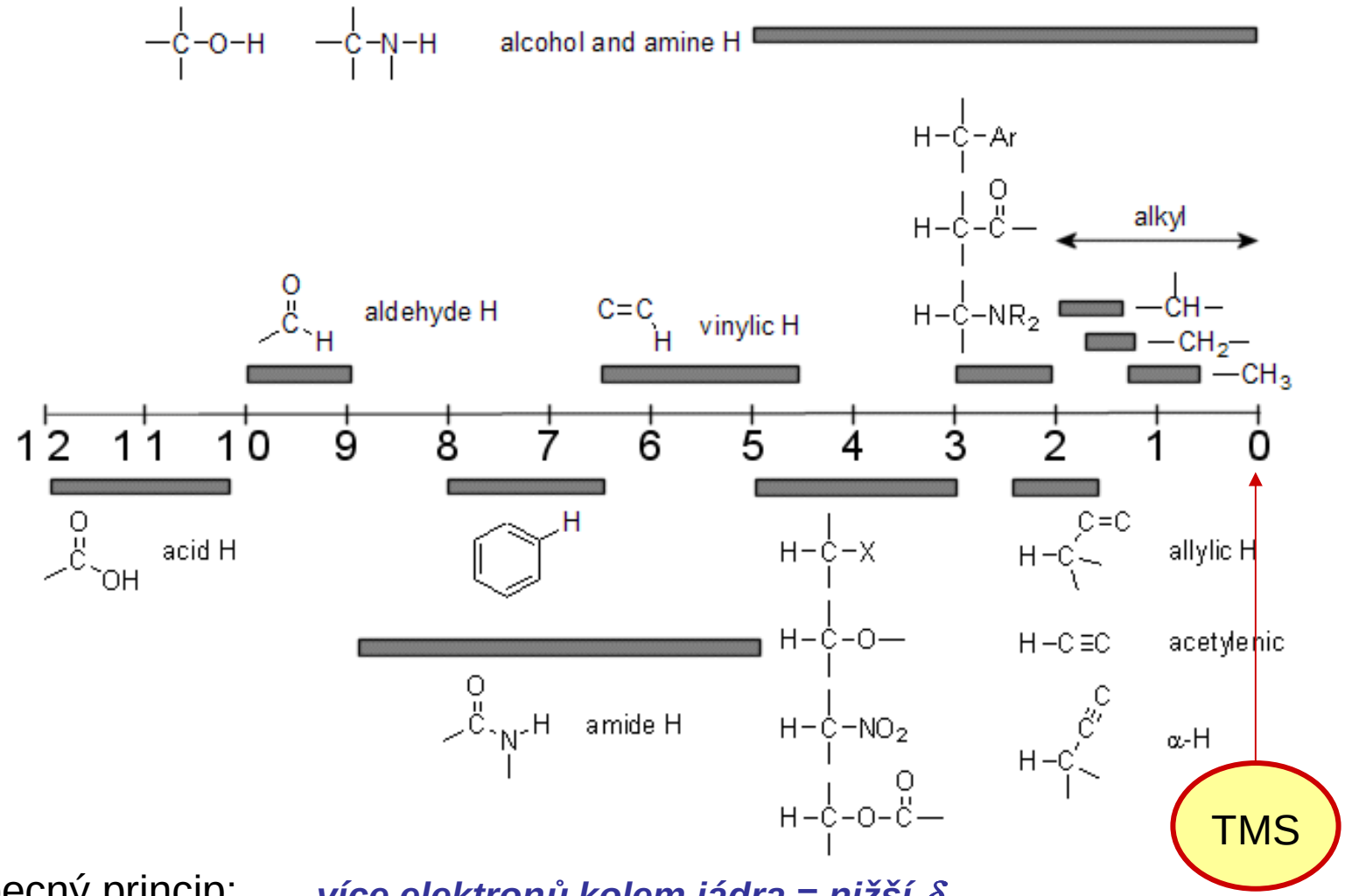


Velké rozdíly v rezonančních frekvencích

–

vždy sledujeme jedno jádro

^{1}H chemické posuny



Obecný princip: ***více elektronů kolem jádra = nižší δ***

http://www.chemistry.ccsu.edu/glagovich/teaching/316/index.html

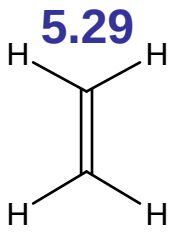
^1H chemické posuny

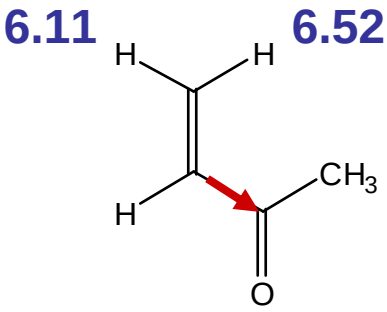
X	$\delta(X\text{-}CH_3)$	elektronegativita
Li	-1	1,0
R_3Si	0	1,8
H	0,4	2,1
CH3	0,8	2,5
NH2	2,36	3,0
OH	3,38	3,5
I	2,16	2,5
Br	2,70	2,8
Cl	3,05	3,0
F	4,25	4,0

deshielding

^{1}H chemické posuny

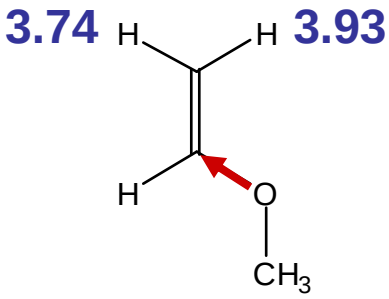
Rezonanční (mezomerní) efekt





elektron-akceptorní

EWG



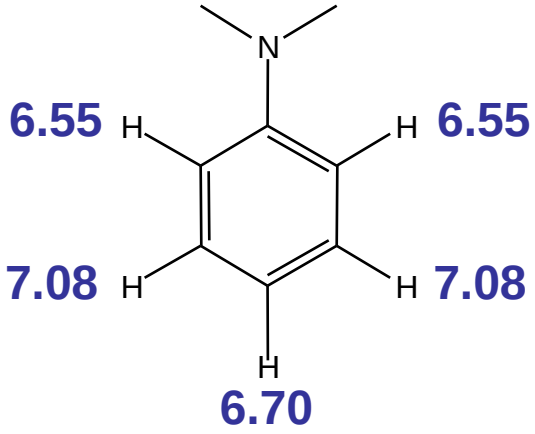
elektron-donorní

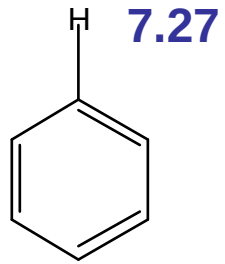
EDG

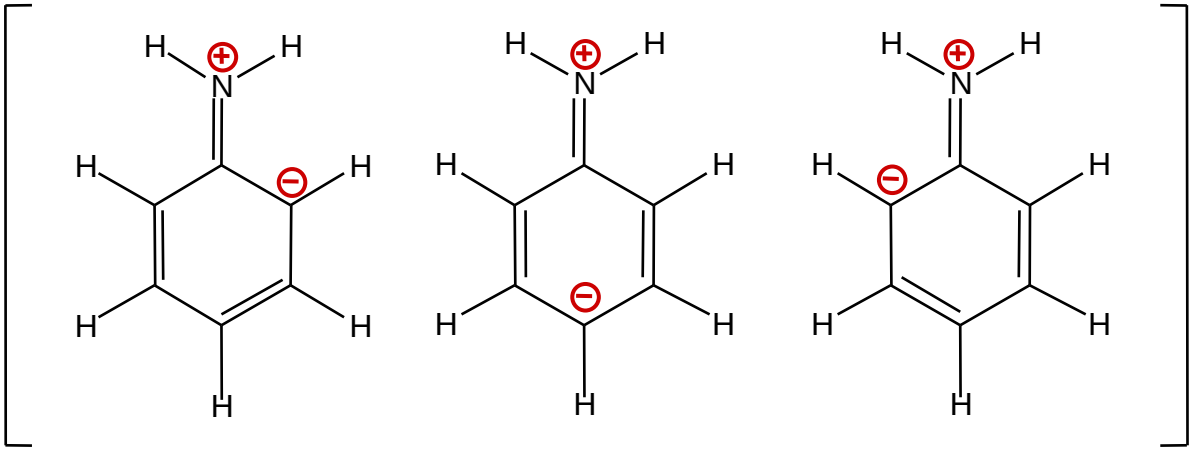
^{1}H chemické posuny

Rezonanční (mezomerní) efekt

+M efekt amino-skupiny



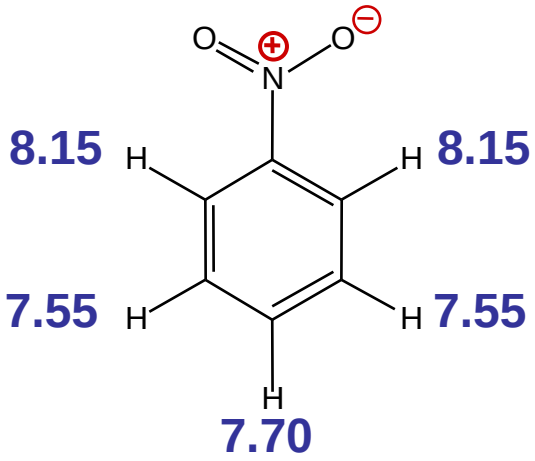


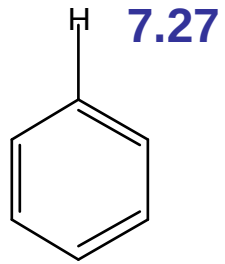


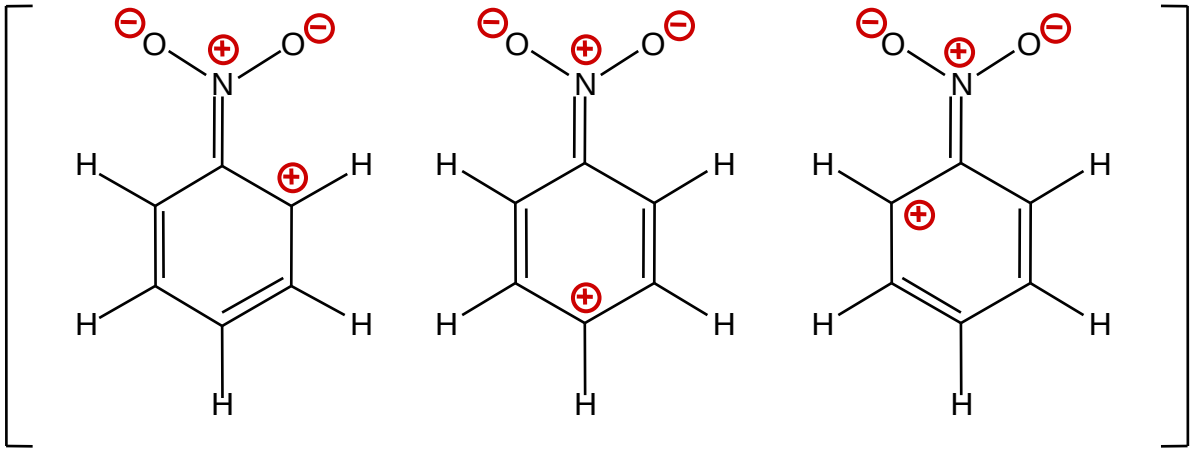
^{1}H chemické posuny

Rezonanční (mezomerní) efekt

-M efekt nitro-skupiny

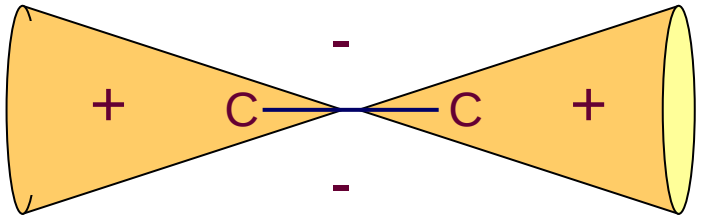






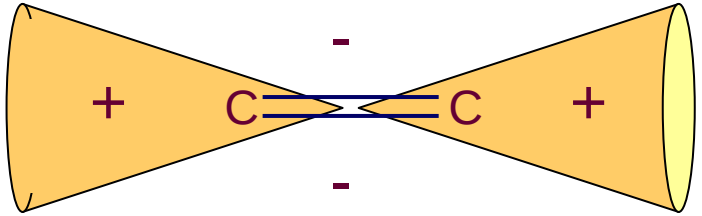
^{1}H chemické posuny

Anizotropní efekt

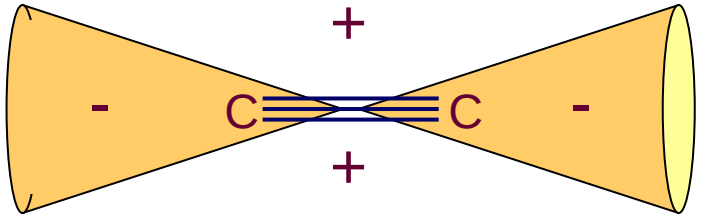


nesymetrické rozložení elektronů

stínící efekt není všude stejný

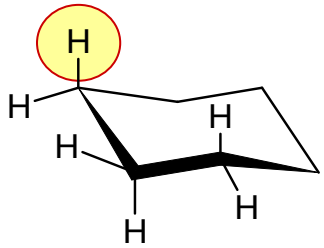


+	vyšší δ
-	nižší δ

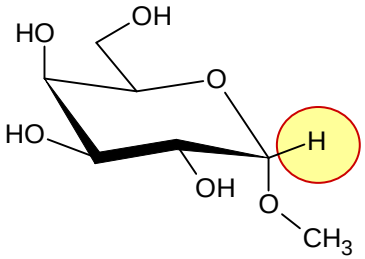


^{1}H chemické posuny

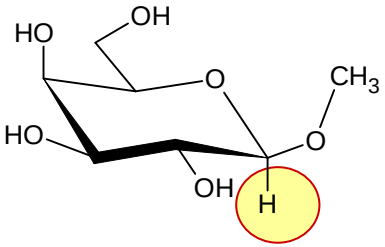
Anizotropní efekt



Axiální vodíky více stíněny (chem. posun o cca 0,5 ppm nižší než ekvatoriální)



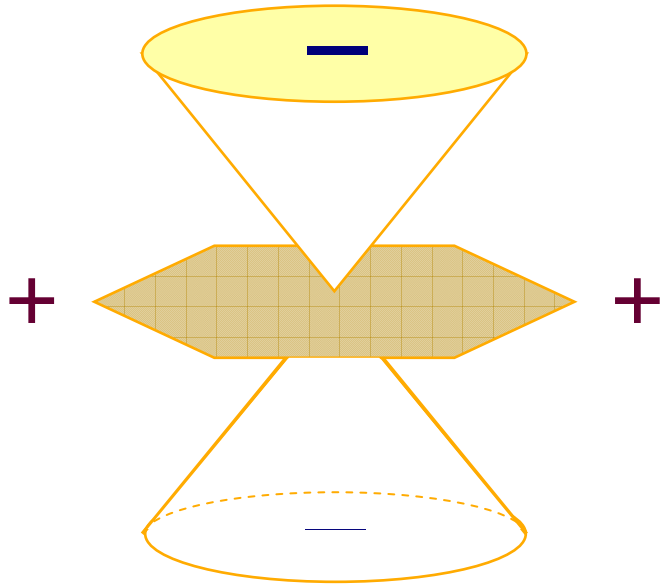
5.18

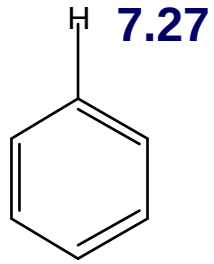


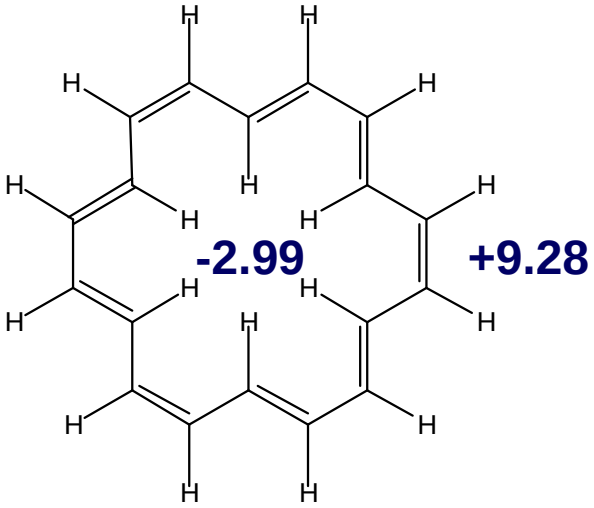
4.69

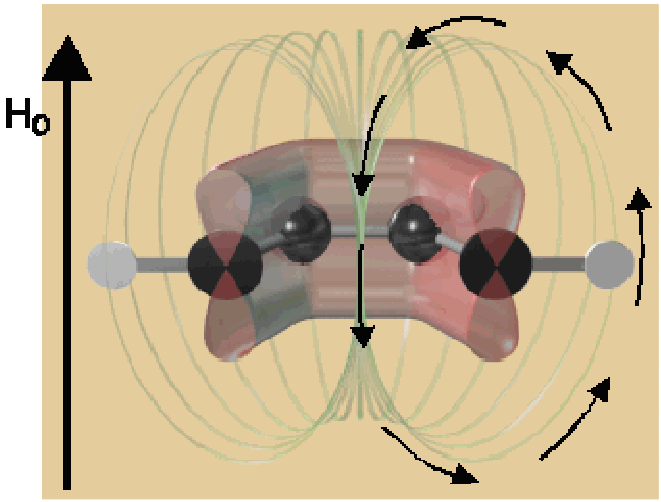
^{1}H chemické posuny

Anizotropní efekt





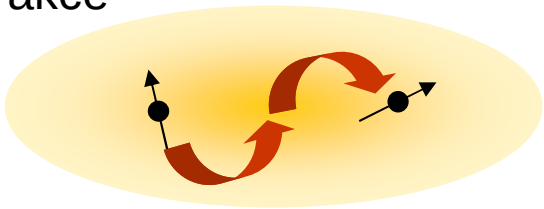




J interakce

Nepřímá spin-spinová interakce

scalar coupling



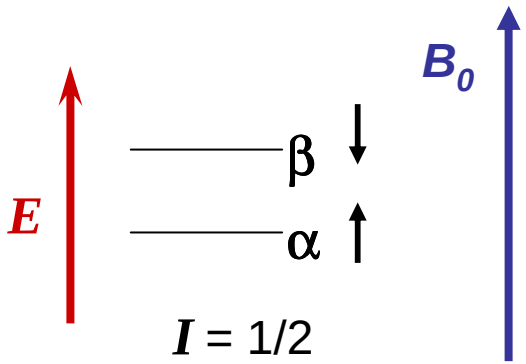
interakce zprostředkovaná vazebnými elektrony

jádro „cítí“ spinový stav okolních jader

K pochopení je třeba kvantová fyzika

Energie magnetického momentu jádra I=1/2 v magnetickém poli

$$E = -\vec{\mu}\cdot\vec{B}$$



$$\Delta E = \hbar\gamma B_0$$

frekvence

pozice signálu ve spektru

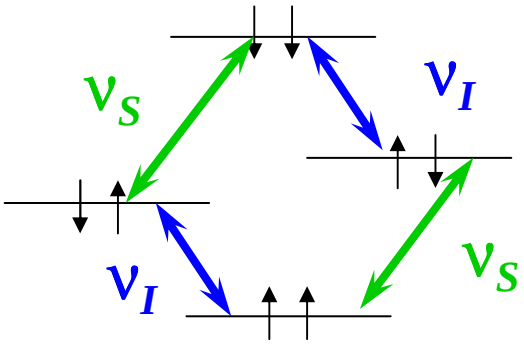
E je kvantována

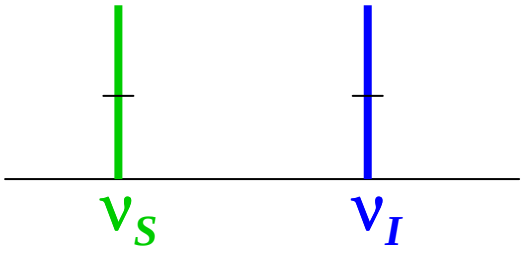
spin ½m může být nalezen jen ve dvou stavech

J interakce

Dvě jádra bez interakce

a s J vazbou

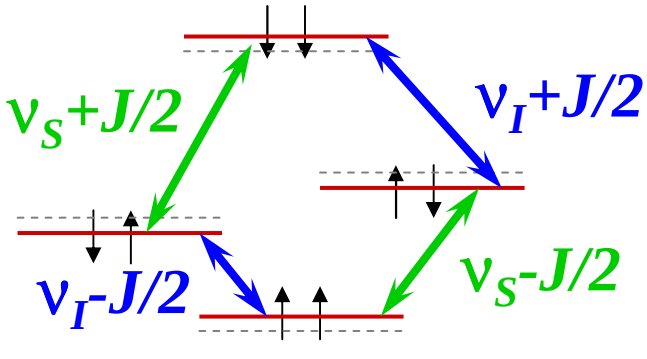


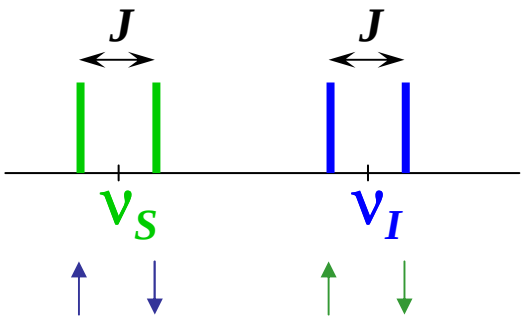


nezáleží na spinu druhého jádra

příspěvek k energii

$E_J = h\, J\, m_I\, m_S$





možné stavy spinu I

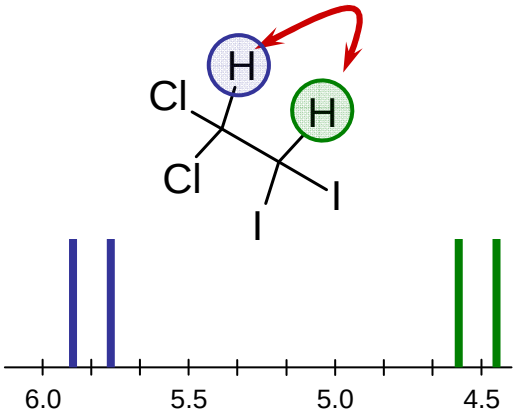
možné stavy spinu S

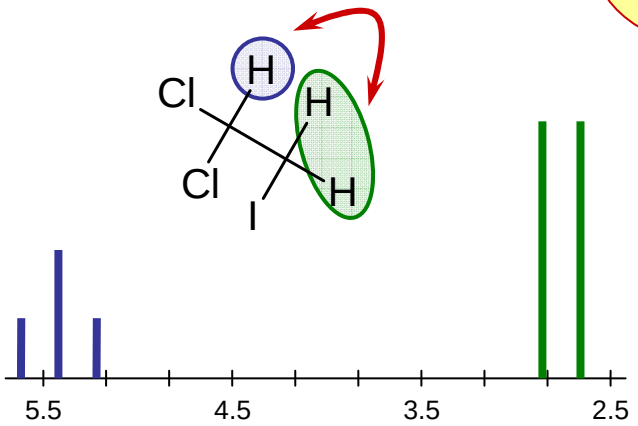
pozice píku je dána rozdílem mezi energetickými hladinami

J vazba v ^{1}H spektrech

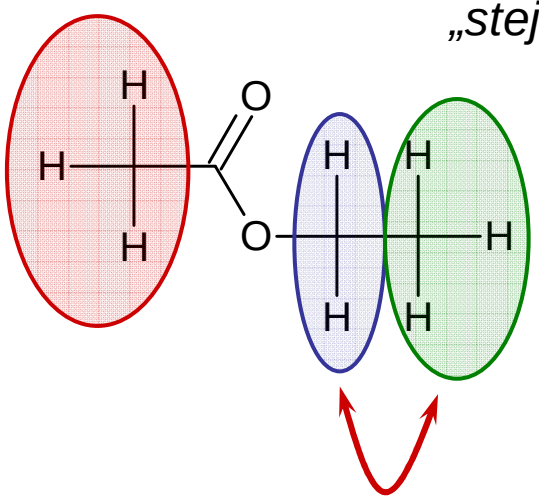
signály jsou štěpeny vodíky, které jsou „různé“

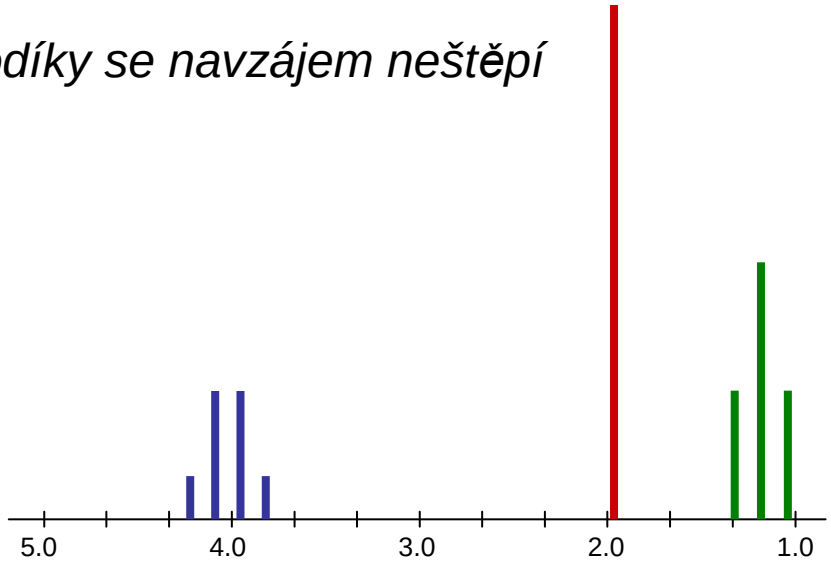
prozatím jen $^{3}J_{HH}$





„stejné“ vodíky se navzájem neštěpí





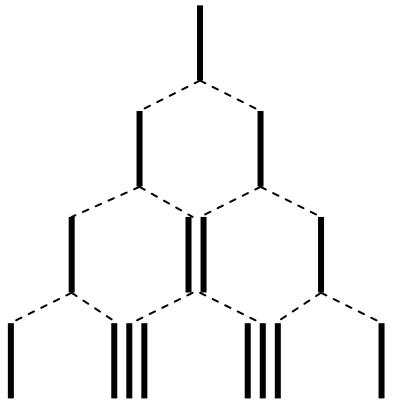
popsat stavy!

J vazba a systém štěpení

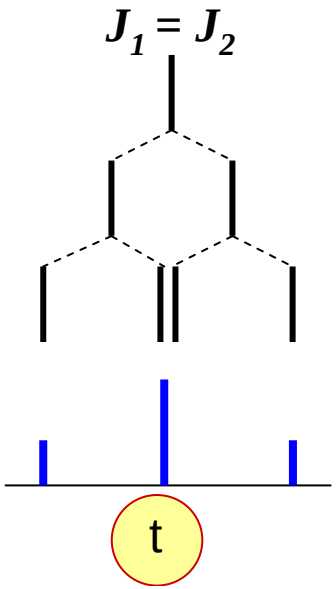
Štěpení ***n*** ekvivalentními vodíky

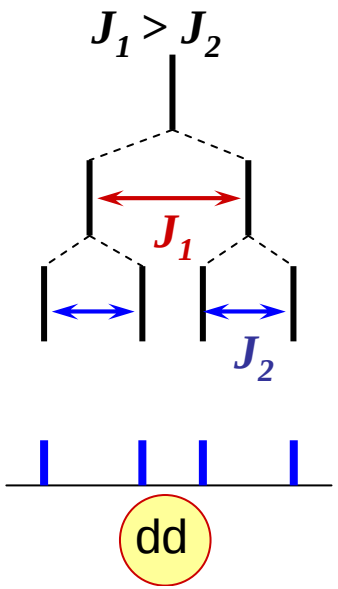
n		
	1	**singlet s**
1	**1 1**	**dublet d**
2	**1 2 1**	**triplet t**
3	**1 3 3 1**	**kvartet q**
4	**1 4 6 4 1**	**pentet p**

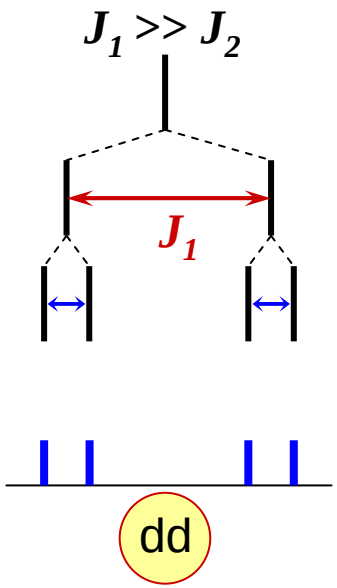
Pascalův trojúhelník



pravidlo n+1

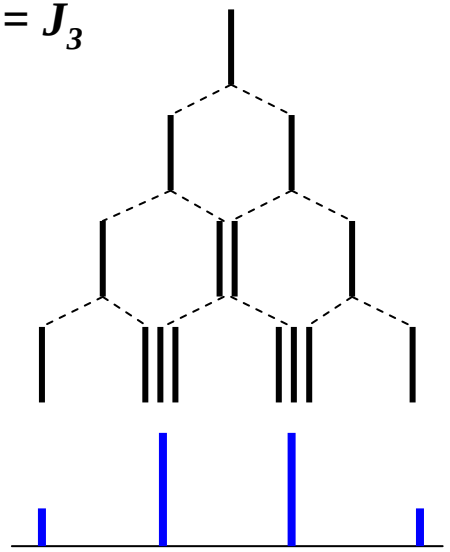






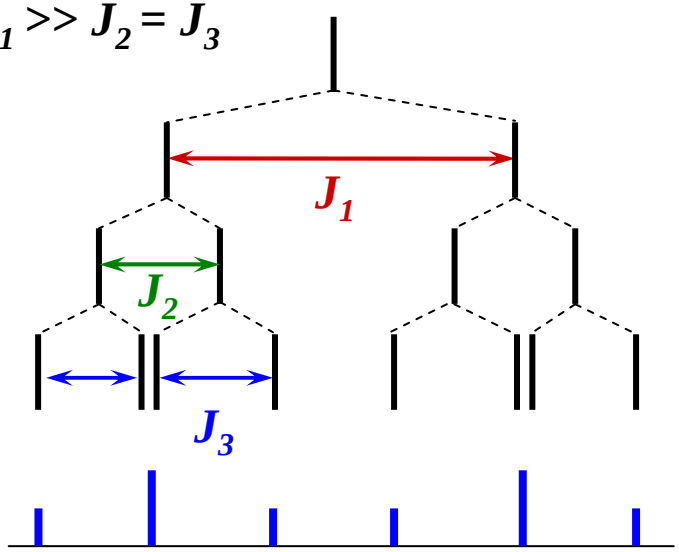
J vazba a systém štěpení

$J_1 = J_2 = J_3$



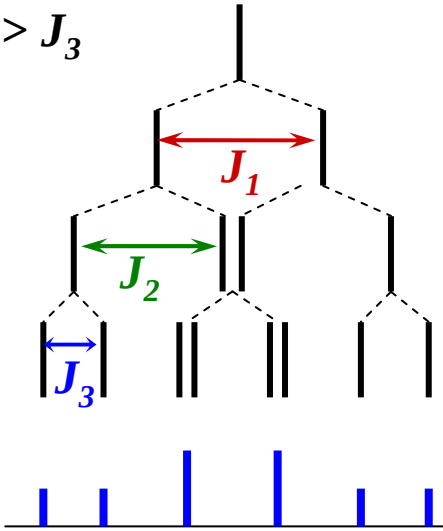
q

$J_1 >> J_2 = J_3$



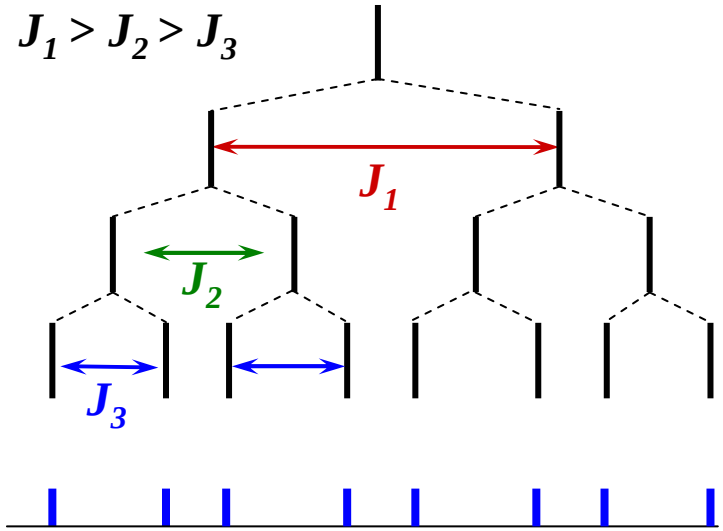
dt

$J_1 = J_2 >> J_3$



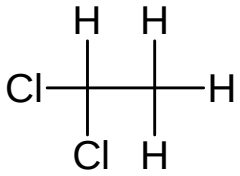
td

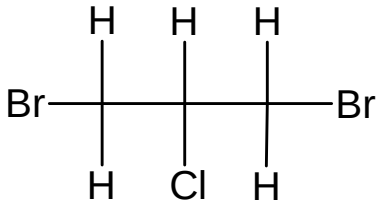
$J_1 > J_2 > J_3$

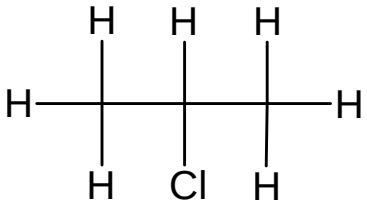


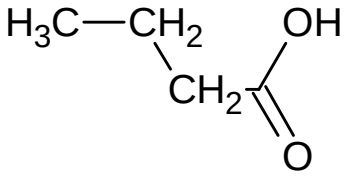
ddd

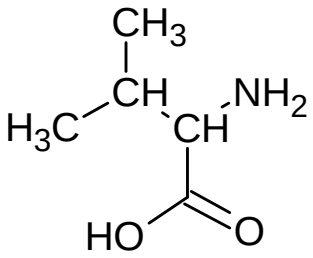
Multiplicita signálů - cvičení

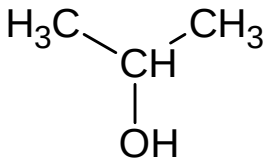






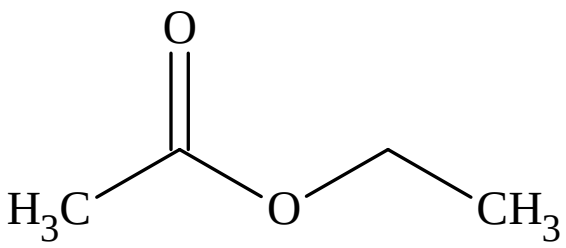






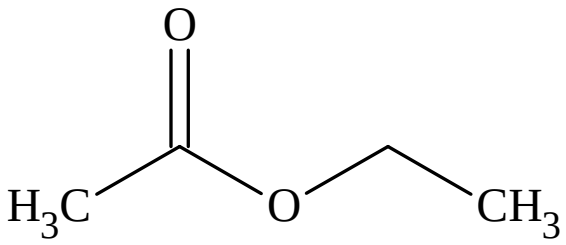
Informace v ^{1}H spektrech

Počet signálů



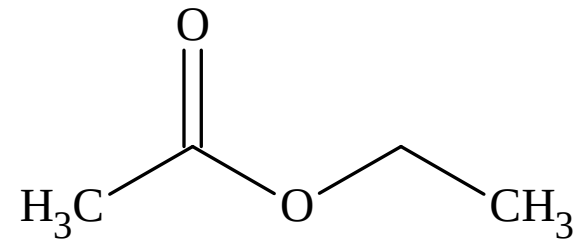
Informace v ^{1}H spektrech

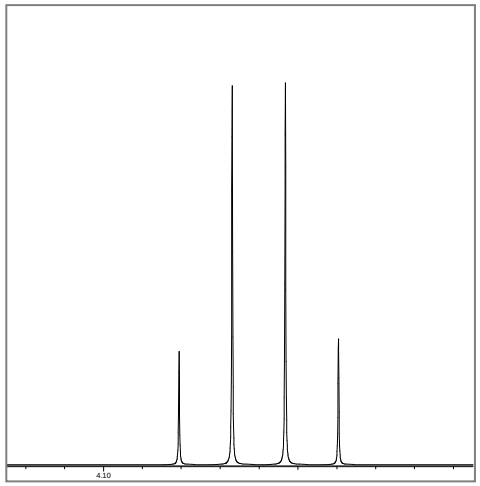
Intenzita signálů

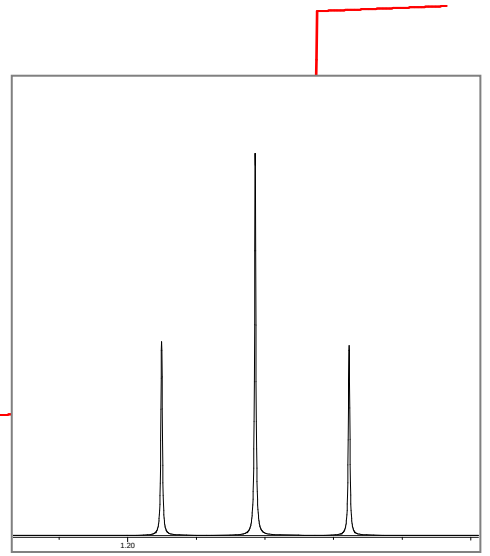


Informace v ^{1}H spektrech

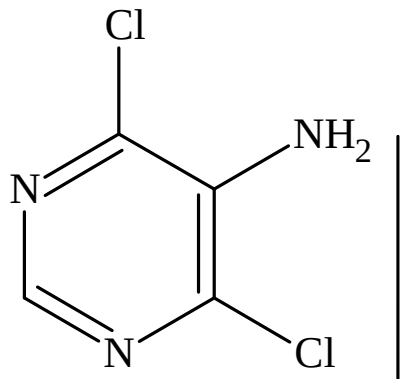
Systém štěpení



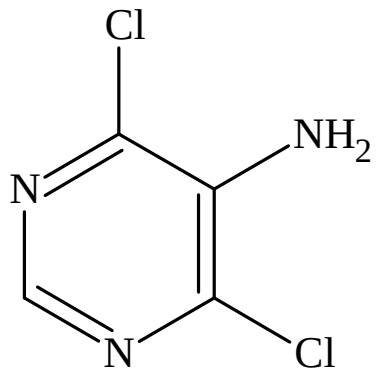




Vyměnitelné vodíky



Vyměnitelné vodíky



+ D_2O

Řešení NMR spektra

Postup

- identifikovat signály, jejich počet, pozici a intenzitu
- rozdělit vodíky do skupin
- analyzovat jemné štěpení, identifikovat jaké skupiny budou vedle sebe
- dokončit identifikaci funkčních skupin s přihlédnutím k chem. posunům a dalším informacím (^{13}C spektrum, APT/DEPT)
- spojit funkční skupiny do molekuly
- znovu ověřit, zda molekula odpovídá spektru