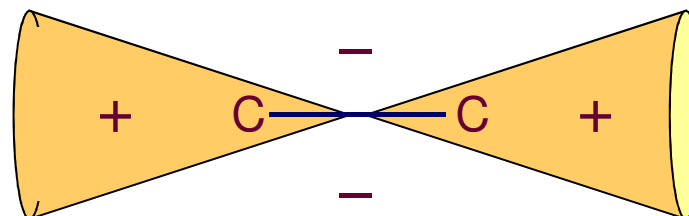

NMR Spektroskopie

Lekce 4: Magnetická anizotropie, spin-spinové interakce

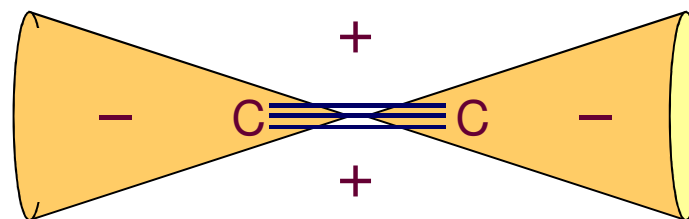
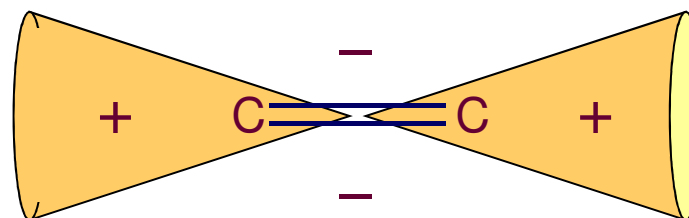


Martin Dračínský

Magnetická anizotropie

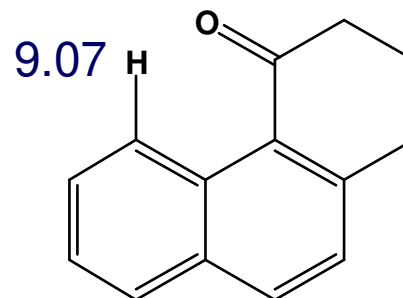
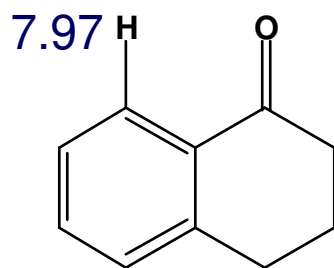
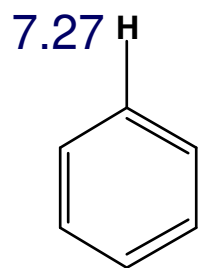
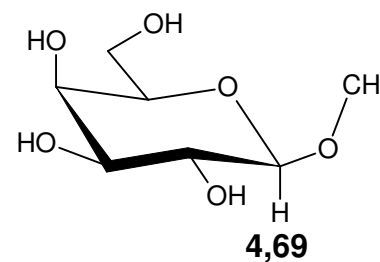
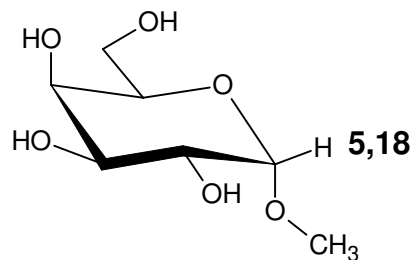
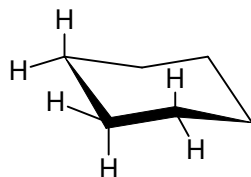


+ vyšší chem. posun
- nižší chem. posun



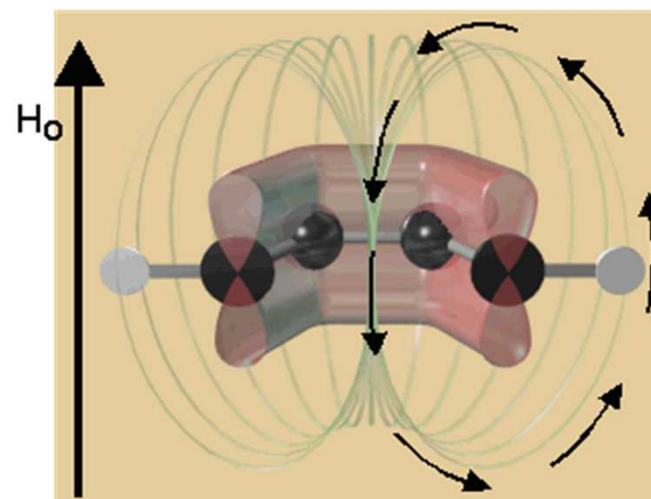
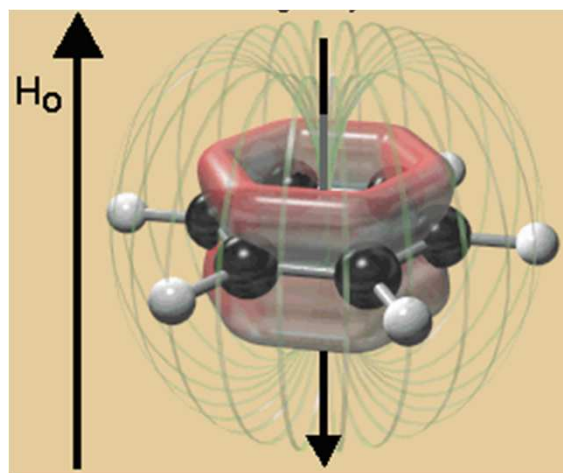
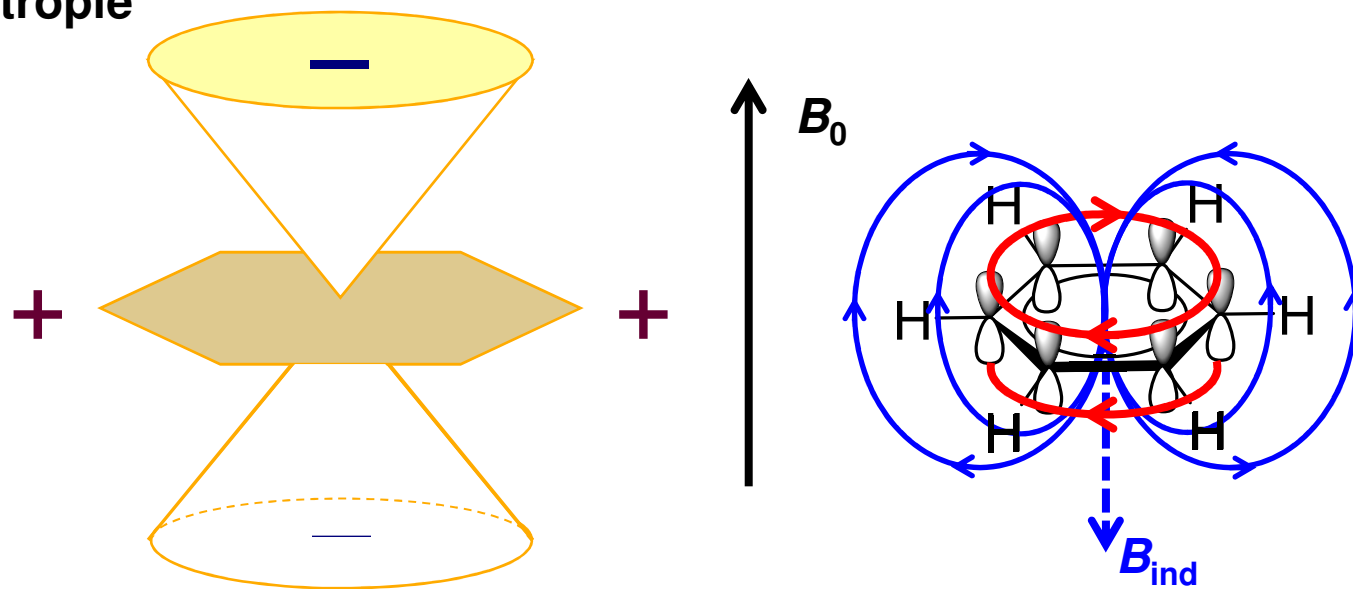
Magnetická anizotropie

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

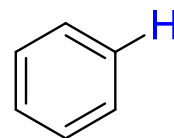
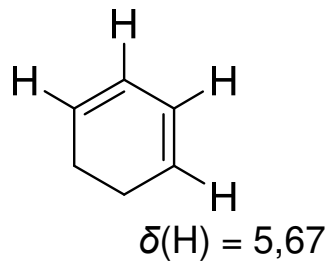


Magnetická anizotropie

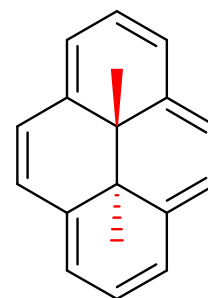
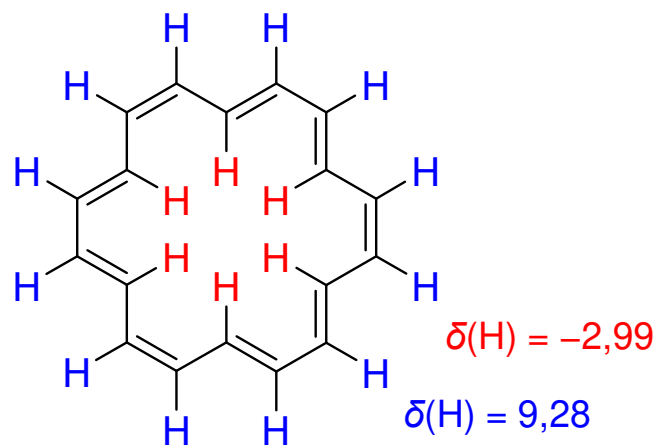
- kruhový proud



$\delta(\text{H}) = 5,78$



$\delta(\text{H}) = 7,27$



$\delta(\text{CH}_3) = -4,25$

Nepřímé spin – spinové interakce

1J

2J geminální

3J vicinální

Interakční konstanty C – H

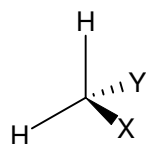
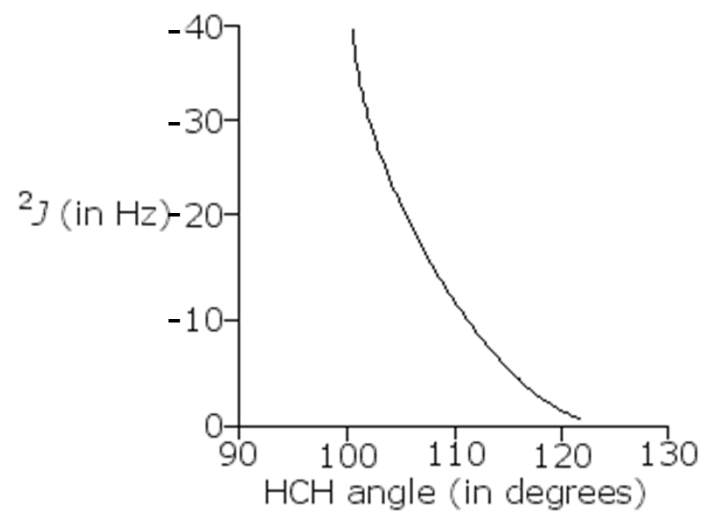
$^1J(\text{C-H}) \approx 5 \times \% \text{ s charakter}$

	$\text{H}_3\text{C-CH}_3$	$\text{H}_2\text{C=CH}_2$	C_6H_6	$\text{HC}\equiv\text{CH}$
$^1J(\text{C-H})$	124,9	156,4	158,4	249,0
Hybridizace	sp^3	sp^2	sp^2	sp
s charakter	25 %	33 %	33 %	50 %

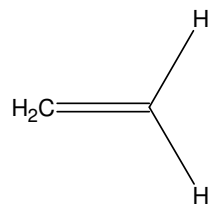
Interakční konstanty H – H

Geminální interakce ${}^2J(\text{H,H})$

- Závislost na vazebném úhlu



$109^\circ \quad J = -12$



$120^\circ \quad J = +3 \text{ až } -3$

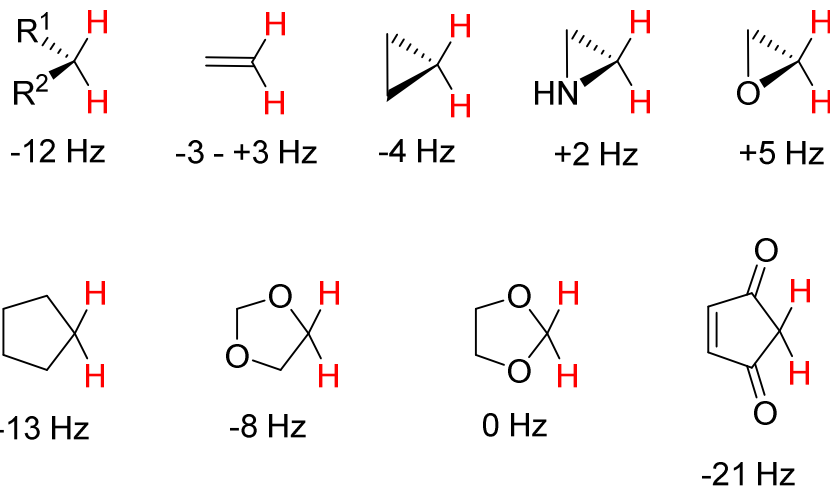
Interakční konstanty H – H

Geminální interakce ${}^2J(\text{H},\text{H})$

- Elektronegativní substituenty mají pozitivní příspěvek

CH_4	CH_3OH	CH_3Cl	CH_3F	CH_2Cl_2
-12,4	-10,8	-10,8	-9,6	-7,5

- Sousedící π elektrony mají negativní příspěvek

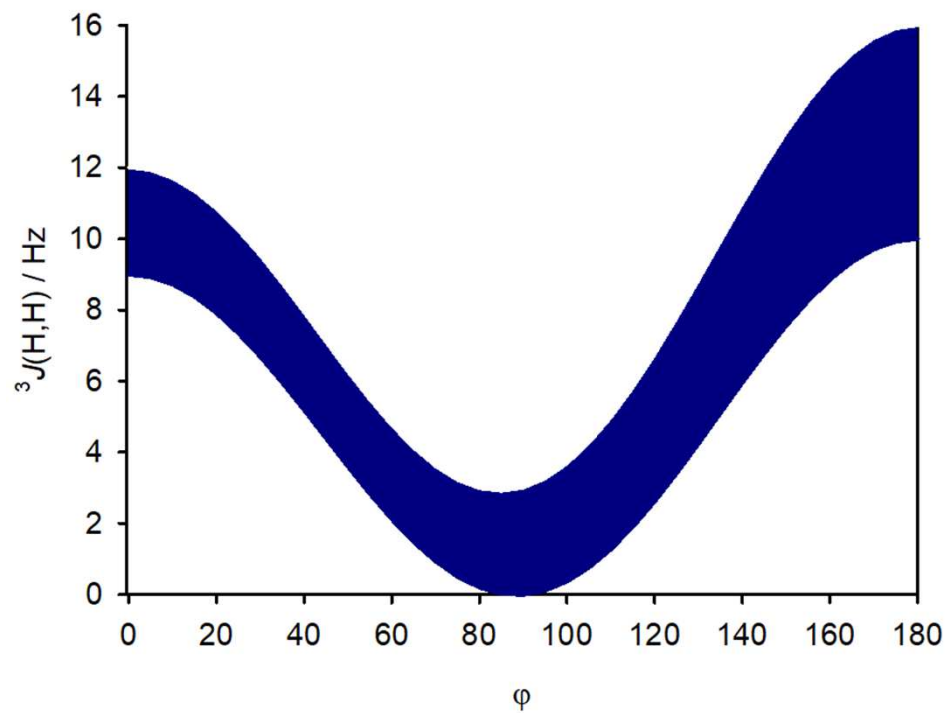


Interakční konstanty H – H

Vicinální interakce ${}^3J(\text{H},\text{H})$

Karplusova křivka

$${}^3J_{\text{HH}} = A \cdot \cos^2(\phi) + B \cdot \cos(\phi) + C$$



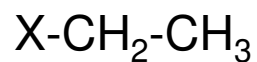
Interakční konstanty H – H

Vicinální interakce ${}^3J(\text{H},\text{H})$

rigidní systémy

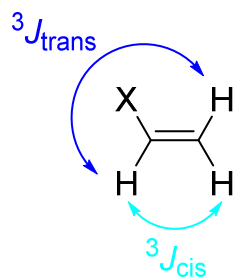
volné otáčení

Elektronegativní substituenty snižují ${}^3J(\text{H},\text{H})$

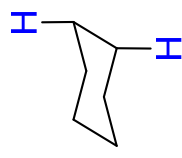


X	Li	H	CH ₃	Cl	OH
${}^3J(\text{H},\text{H})$	8,4	8,0	7,3	7,2	6,9

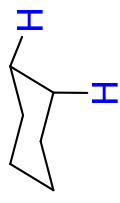
$J(\text{trans}) > J(\text{cis})$



X	Li	H	Cl	OMe	F
${}^3J(\text{cis})$	19,3	11,6	7,3	7,1	4,7
${}^3J(\text{trans})$	23,9	19,1	14,6	15,2	12,8



10-13 Hz



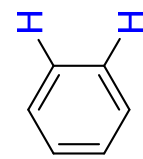
2-4 Hz



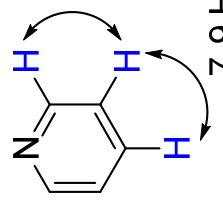
2-4 Hz



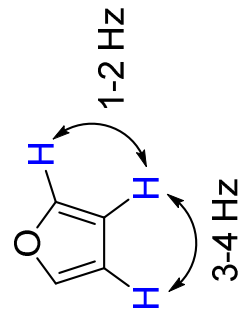
6-8 Hz



7-8 Hz

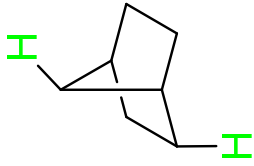


5-6 Hz



1-2 Hz

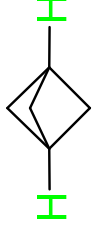
3-4 Hz



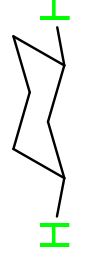
3-4 Hz



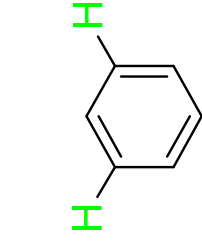
10 Hz



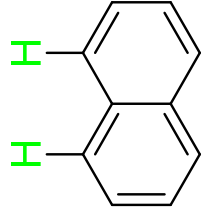
18 Hz



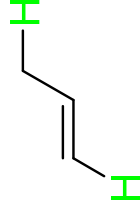
1-3 Hz



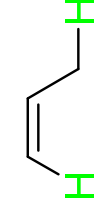
1-3 Hz



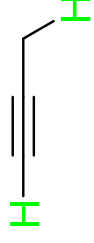
0,7 Hz



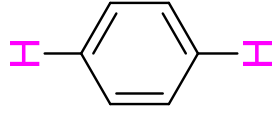
1-3 Hz



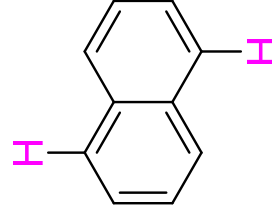
1-3 Hz



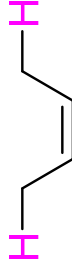
2-3 Hz



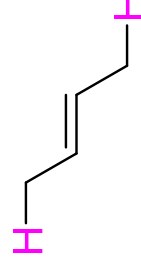
0,7 Hz



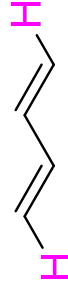
0,8 Hz



1-3 Hz



1-3 Hz



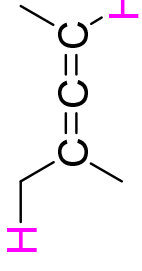
1,3 Hz



0,6 Hz



2-3 Hz



3 Hz