

C8953
NMR strukturní analýza
seminář

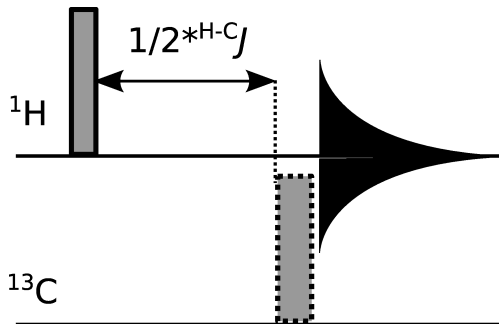
Úvod do 2D NMR & Homonukleární korelace

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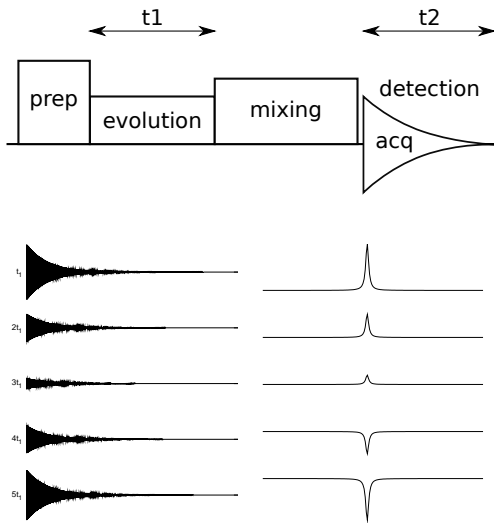
21. března 2012

Vektorový model

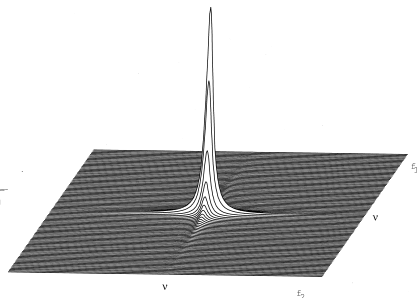
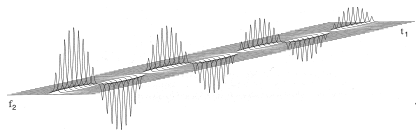


Druhá dimenze f_1

- ▶ přípravná perioda \implies koherence
- ▶ vývojová perioda $t_1 \xrightarrow{FT} f_1$
 - ▶ inkrementy
 - ▶ vývoj koherence
- ▶ směšovací perioda (mixing)
 - ▶ kódování frekvencí
 - ▶ vytvoření měřitelného signálu
- ▶ detekce signálu $t_2 \xrightarrow{FT} f_2$



2D NMR

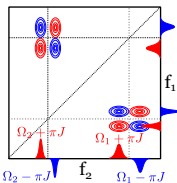
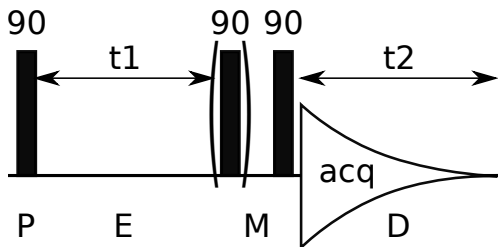


2D spektrum

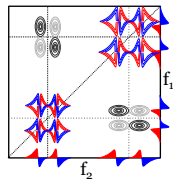
- ▶ FT v t_1 - modulovaná 1D spektra
- ▶ FT v t_2 - 2D spektrum

COSY

- ▶ nejjednodušší 2D experiment
- ▶ koreluje jádra ma základě $2/3 J$
- ▶ přes 2, 3, (4) vazby
- ▶ antifázové kroszíky
- ▶ DQF-COSY - absorpční tvar diagonály

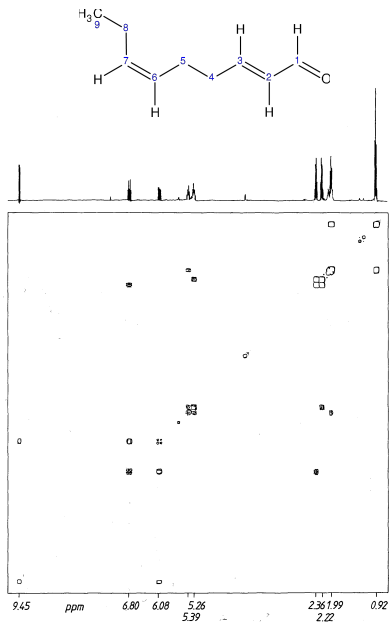


$$1/2[\cos(\Omega t_1 + \pi J t_1) - \cos(\Omega t_1 - \pi J t_1)]$$

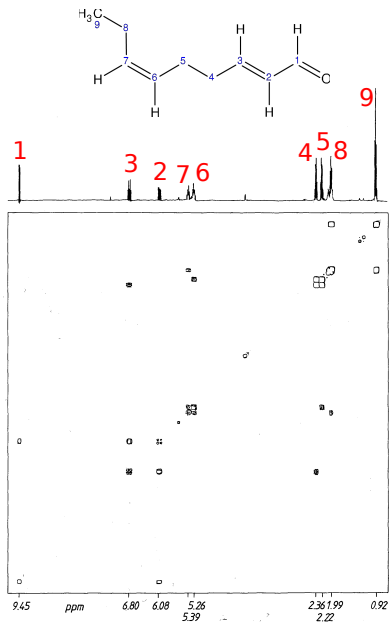


$$1/2[\sin(\Omega t_1 + \pi J t_1) + \sin(\Omega t_1 - \pi J t_1)]$$

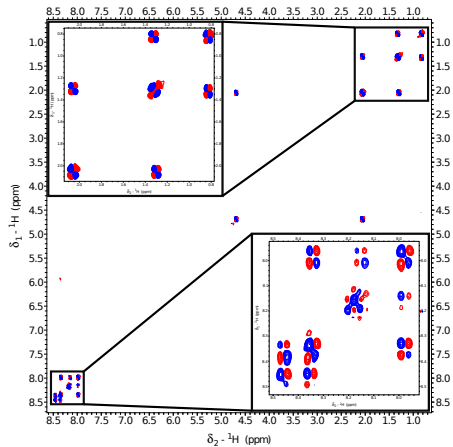
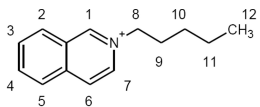
COSY 1



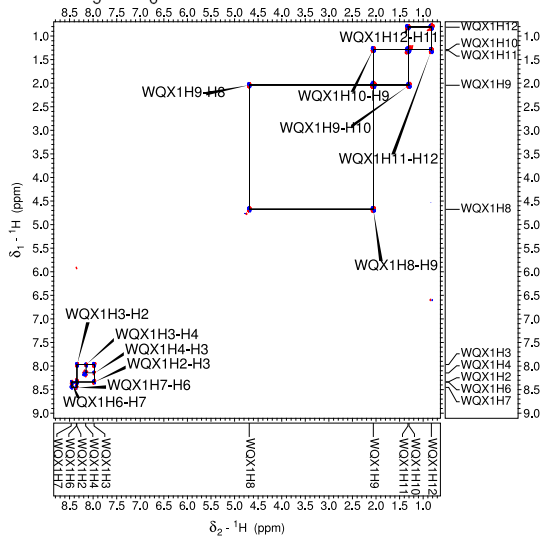
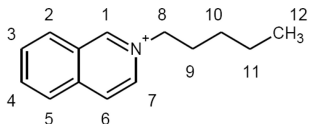
COSY 1



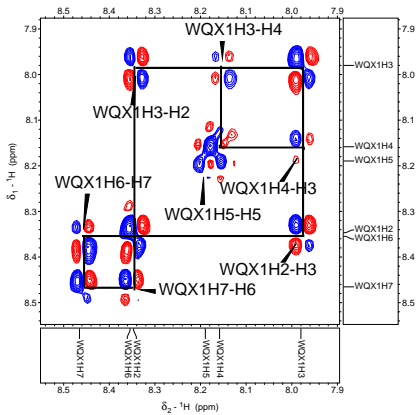
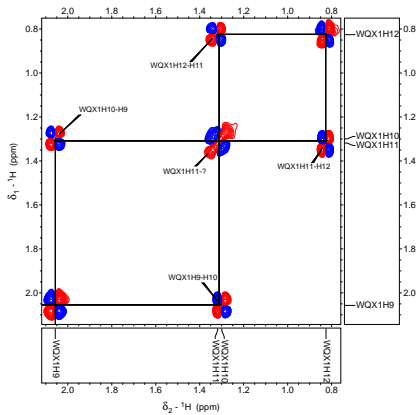
COSY 2



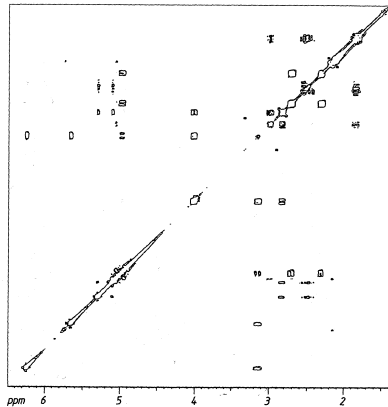
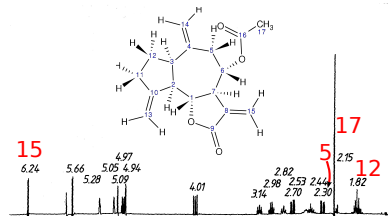
COSY 2



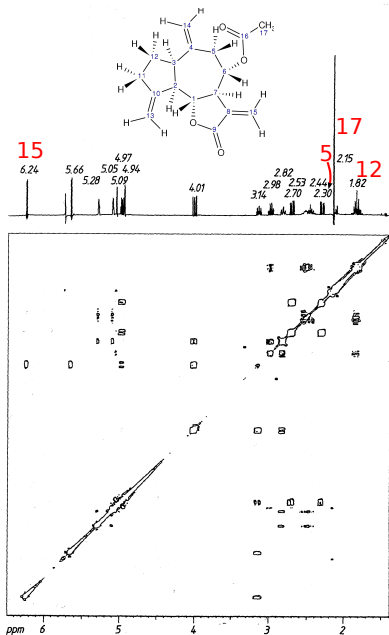
COSY 2



COSY 3



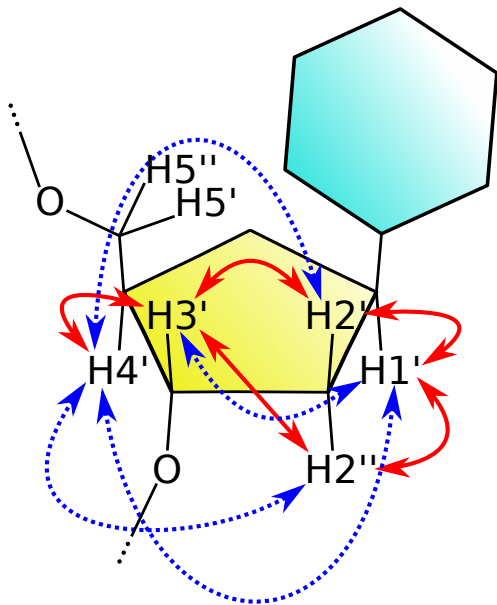
COSY 3



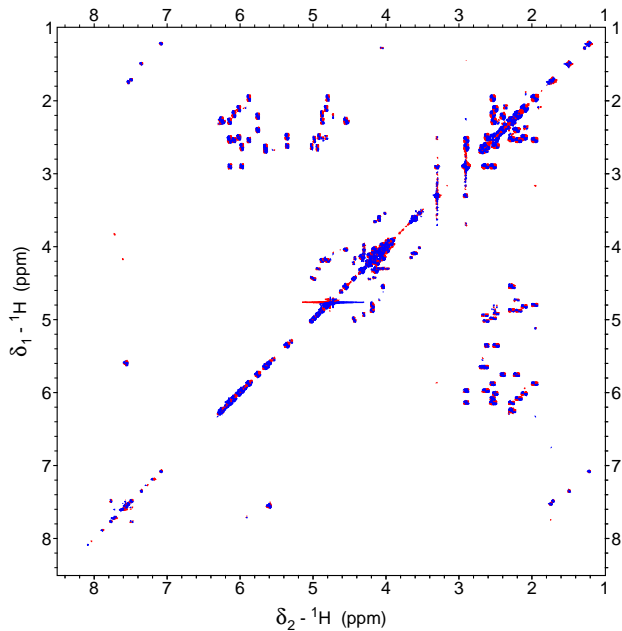
atom/skupina	δ ppm
H1	4.01
H2	2.82
H3	2.98
H5, H5'	2.30, 2.70
H6	4.97
H7	3.14
H11, H11'	2.44, 2.53
H12, H12'	1.80, 1.84
H13, H13'	5.09, 5.28
H14, H14'	4.94, 5.05
H15, H15'	6.24, 5.66
H17	2.15

COSY v nukleových kyselinách

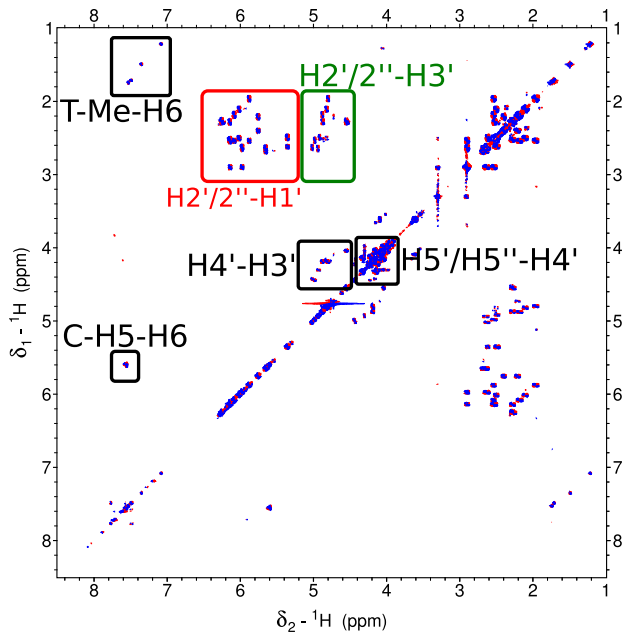
- ▶ COSY
- ▶ TOCSY



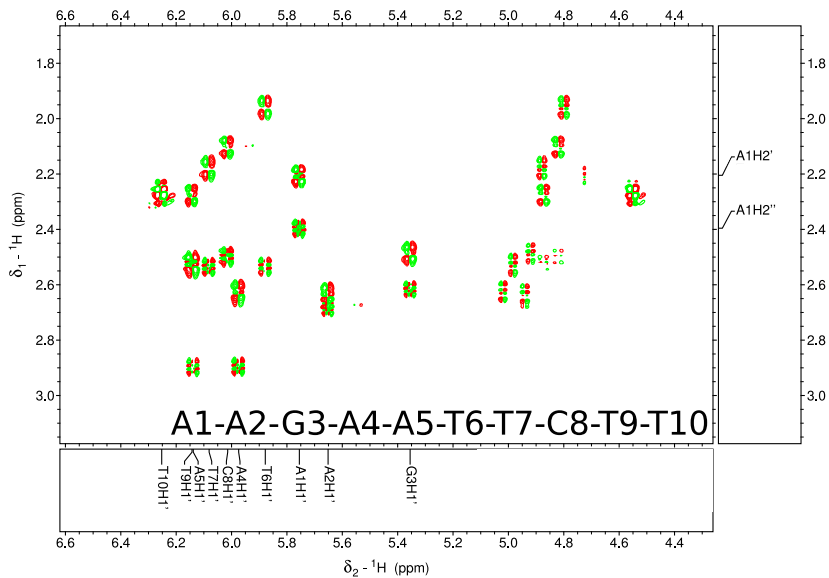
$d(\text{AAGAATTCTT})_2$ v D_2O , DQF-COSY



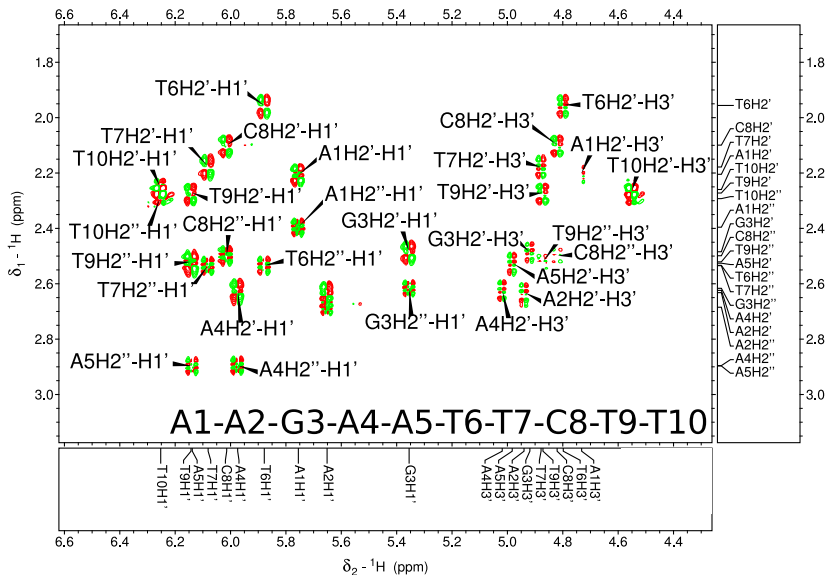
d(AAGAATTCTT)₂ v D₂O, DQF-COSY



H2'/2"-H1', H2'/H2"-H3'



H2'/2''-H1', H2'/H2''-H3'



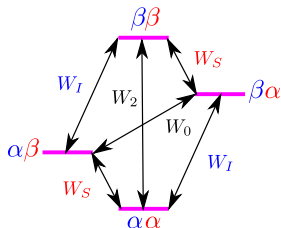
NOESY - úvod

Nukleární Overhauserův efekt

- ▶ dipól-dipólové interakce
- ▶ transfer magnetizace přes prostor způsobený cross-relaxací

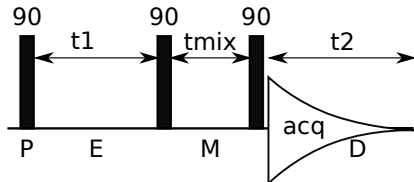
NOESY

- ▶ koreluje jádra vzdálená méně než cca 5 Å

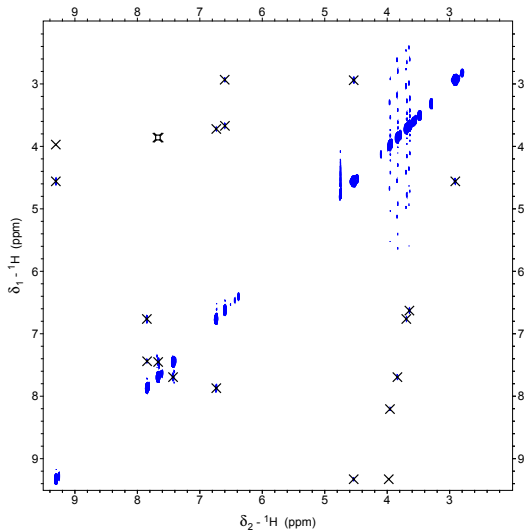
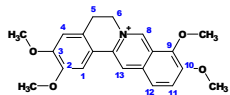


$$\frac{d\Delta I_z}{dt} = -\rho_I(I_z - I_z^0) - \sigma_{IS}(S_z - S_z^0)$$

$$\sigma_{IS} = W_2 - W_0$$



NOESY malých molekul



NOESY malých molekul

