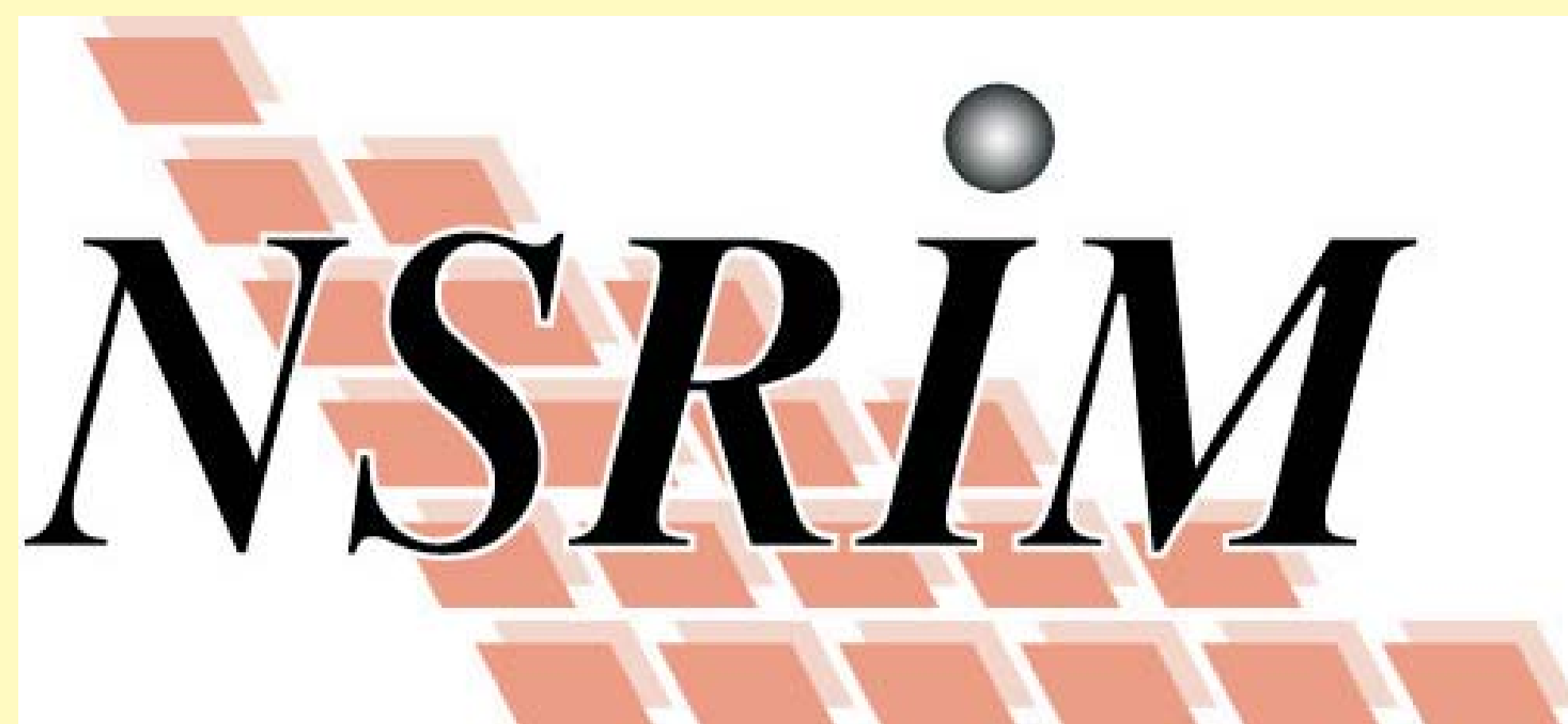


# Solid-State NMR Studies of Environmentally Friendly Flame Retardants



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## Introduction

For many applications, polymer based materials have to pass fire retardance tests. Frequently, halogenated compounds are used as fire retardant additives, which suffer from the disadvantage of being environmentally hazardous under the influence of heat. Therefore it is of great interest to develop environmentally friendly flame retardants, which may be incorporated into polymers. A promising group of flame retardants is considered to be melamine phosphates (MP). An important goal to improve flame retardants is to relate their chemical composition and structure to their mechanism of functioning.

In a first step the approximate powder structure of MP was obtained by X-ray diffraction. Although the proton positions cannot be determined by X-ray diffraction, alternative models were proposed using a combined molecular modeling-Rietveld refinement approach. Although one model was favored, no conclusive answers could be drawn. A key issue is if and how the protons from the phosphoric acid bind to the melamine moiety.

mine moiety.

<sup>1</sup>H solid-state NMR is the ideal tool to gain detailed information about the proton positions, proximities and the hydrogen bonding network.

Here we present solid-state NMR results which include high resolution <sup>1</sup>H spectra obtained under magic-angle-spinning (MAS) conditions and different types of heteronuclear correlation spectra (<sup>1</sup>H-<sup>13</sup>C, <sup>1</sup>H-<sup>31</sup>P, <sup>1</sup>H-<sup>15</sup>N) obtained on <sup>13</sup>C and <sup>15</sup>N enriched MP.

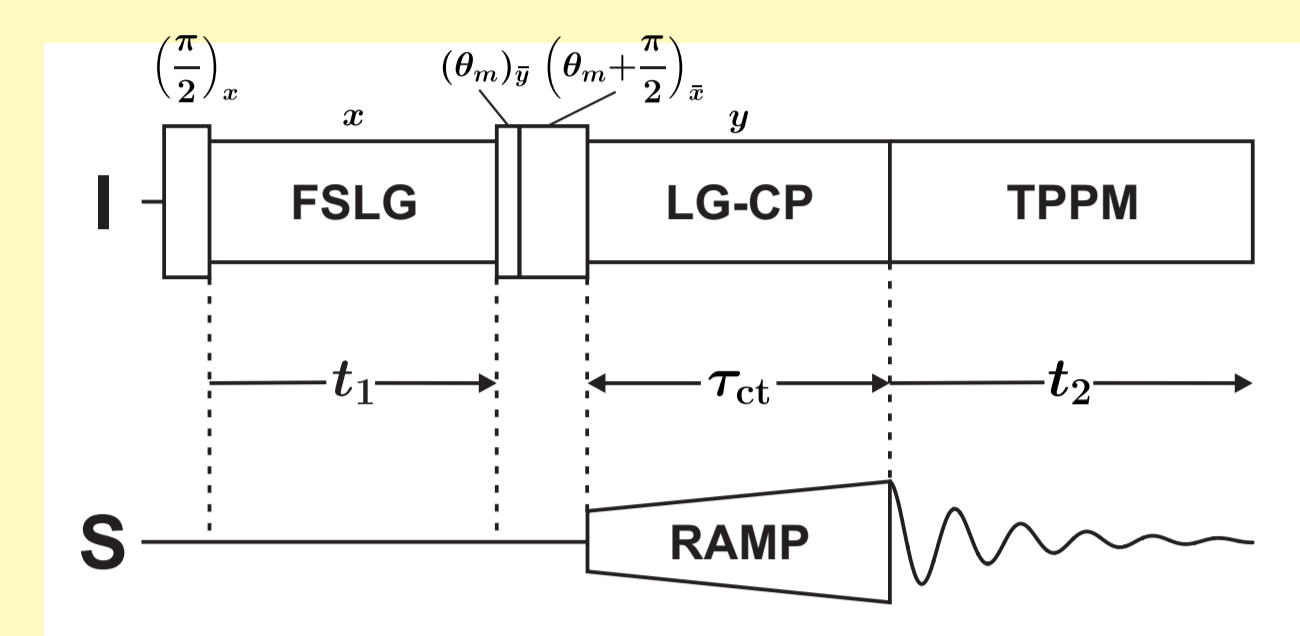
The solid-state NMR results confirm in parts the model for the proton positions obtained from the combined molecular modeling-Rietveld refinement approach.

In addition we present first results obtained on melamine pyrophosphates (M<sub>2</sub>P<sub>2</sub>) and melamine polyphosphates (MPpoly).

## Methods

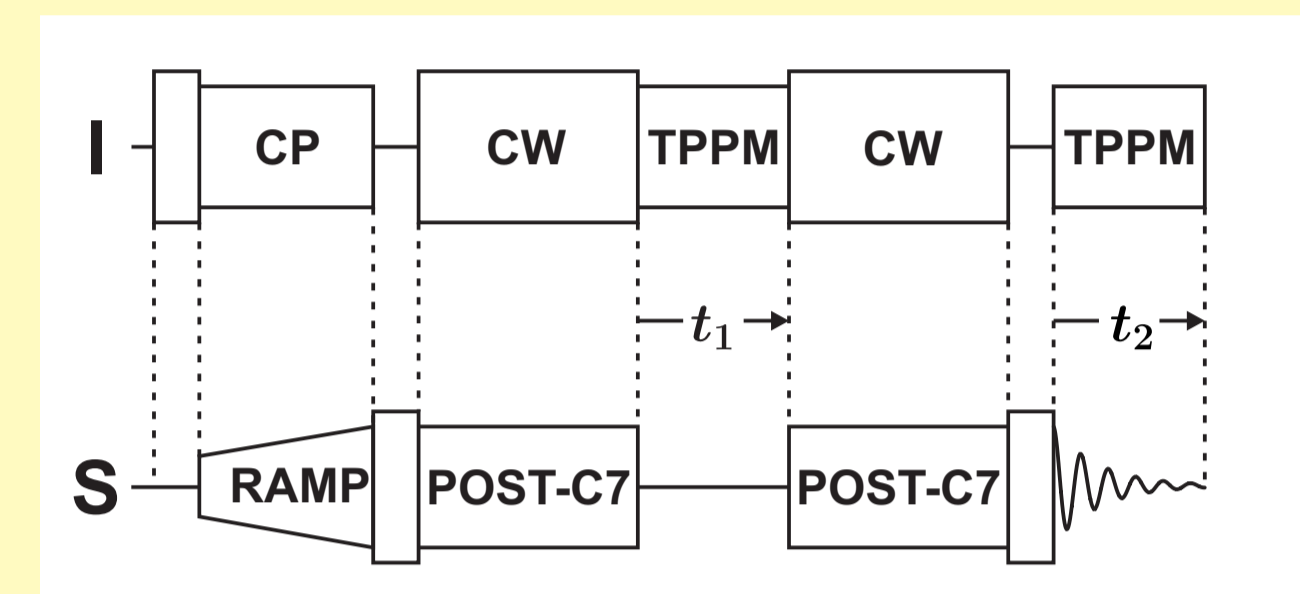
### Heteronuclear Correlation Spectra (HETCOR):

After the FSLG homonuclear decoupling sequence is applied to the I spins (<sup>1</sup>H) in the t<sub>1</sub> dimension, the magnetization is transferred to the S-spins (<sup>13</sup>C, <sup>31</sup>P, <sup>15</sup>N) by Lee-Goldburg cross-polarization (LG-CP), during which the <sup>1</sup>H spins are homonuclear decoupled [3]. The ω<sub>1</sub> axis in the resulting 2D spectra represents the high resolution <sup>1</sup>H dimension, while the ω<sub>2</sub> axis represents the direct S dimension. Cross-peaks indicate close heteronuclear through-space I-S contacts.



### Homonuclear Double-Quantum Spectra:

After ramped cross-polarization, the enhanced longitudinal S-spin (<sup>15</sup>N) magnetization is converted into homonuclear double-quantum coherences using the POST-C7 homonuclear double-quantum recoupling sequence. The double-quantum coherences evolve during the interval t<sub>1</sub> and are converted back into observable magnetization, which is detected in the interval t<sub>2</sub>.



## Results

The 1D <sup>1</sup>H spectrum was obtained in an external field of 18.8 T and a spinning frequency of 50 kHz.

All 2D experiments were performed at a field of 7.1 T and a spinning frequency of 12 kHz.

The proton resolution in the 2D spectra is different in the different correlation experiments. This shows the advantage of the heteronuclear correlation experiments compared to pure proton spectra.

The proton resolution can be improved by using different homonuclear decoupling sequences. Tests on alanine using PMLG [2] and R182<sup>9</sup> [4] did not show an improved resolution. However it is expected that these sequences

result in better resolution at high external fields (≈18 T) combined with high rf fields (≈200 kHz) [2].

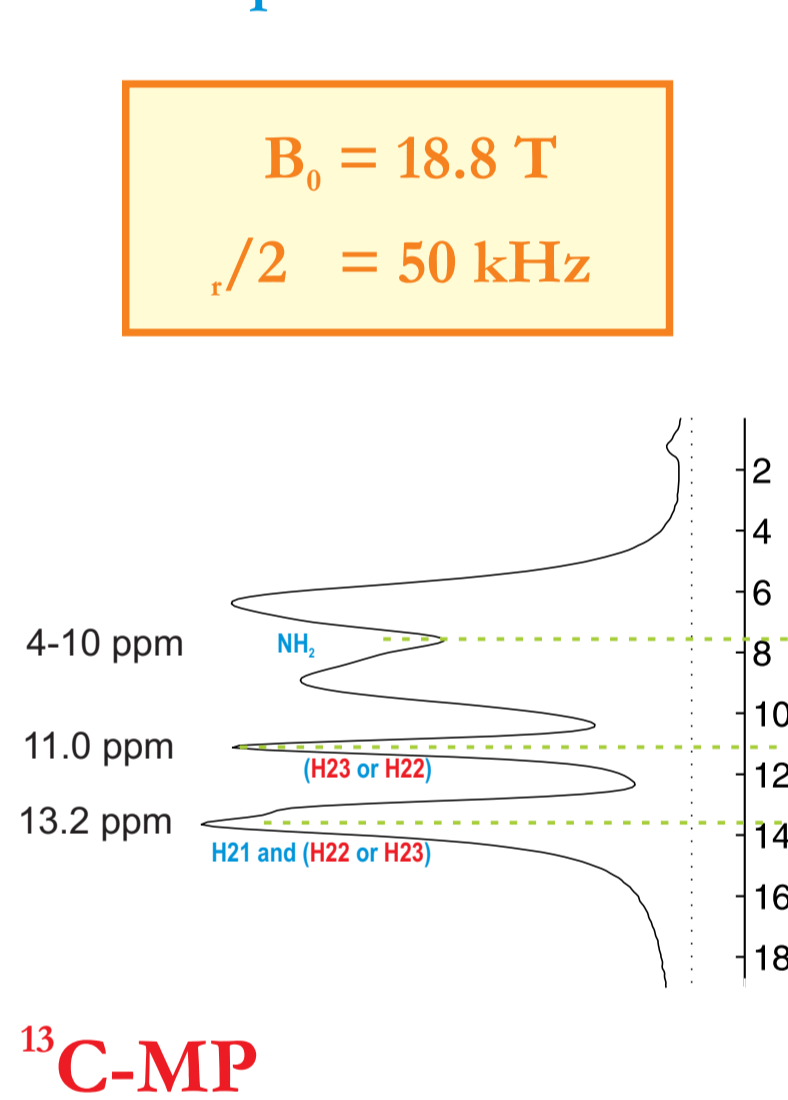
### <sup>15</sup>N-<sup>15</sup>N 2D Double-Quantum Spectrum:

On the right a 2D <sup>15</sup>N-<sup>15</sup>N double-quantum spectrum of <sup>15</sup>N-MP is shown. The spectrum was recorded at a field of

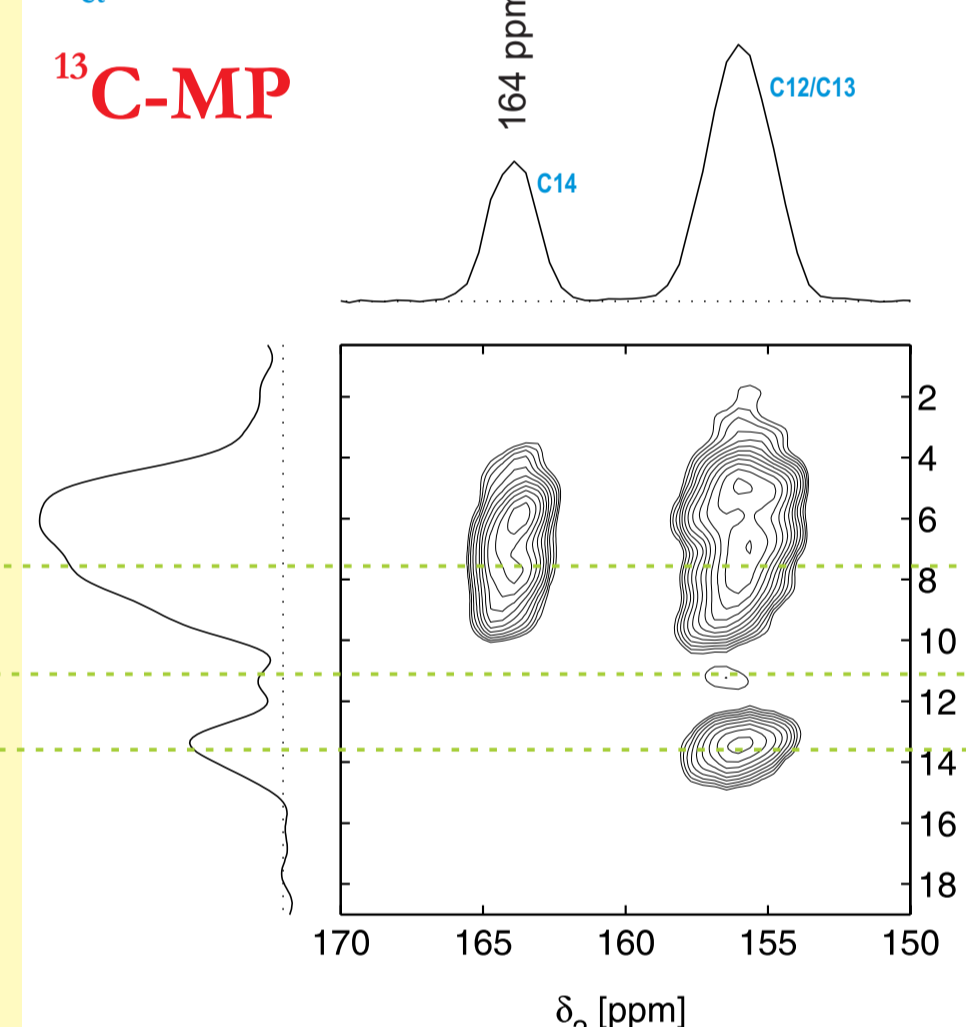
7.1 T and a spinning frequency of 6.056 kHz.

The assignment of the <sup>15</sup>N resonances is indicated. The resonances for the N9/N10 and N6/N7 sites could not be uniquely assigned.

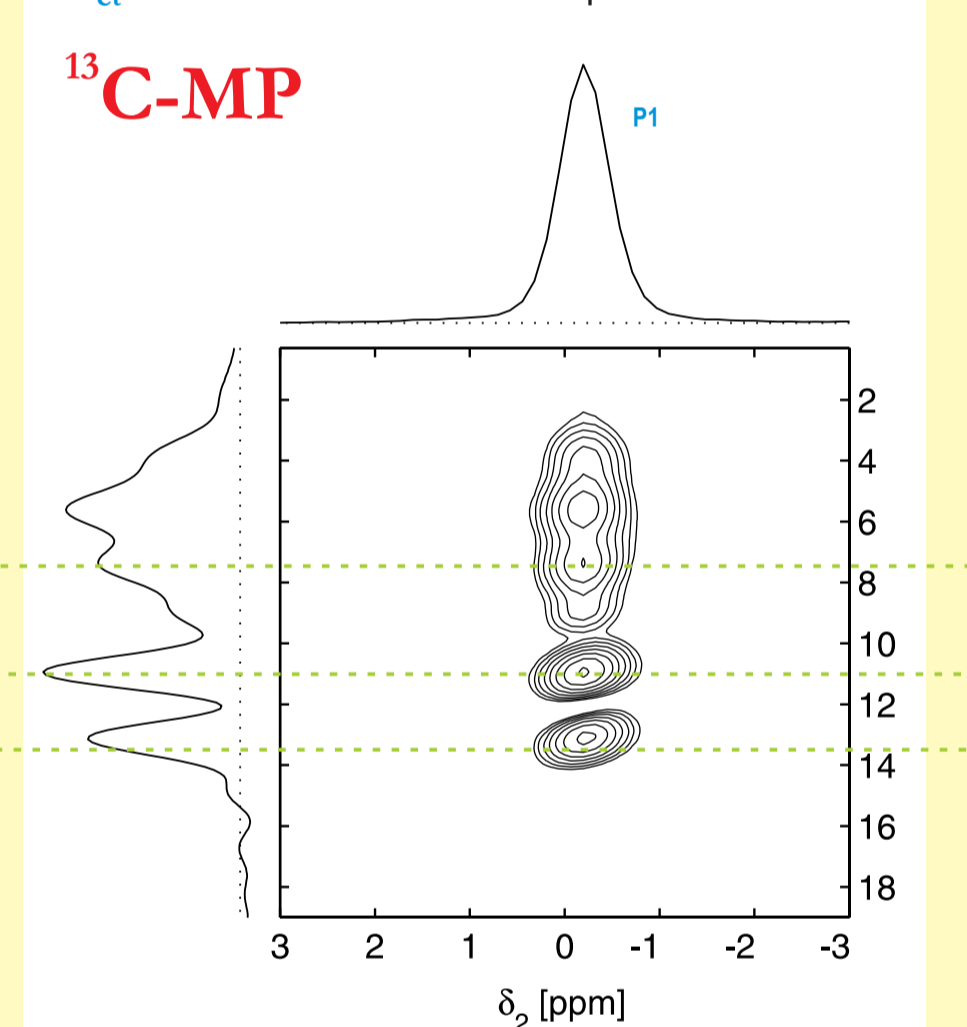
### 1D <sup>1</sup>H Spectrum



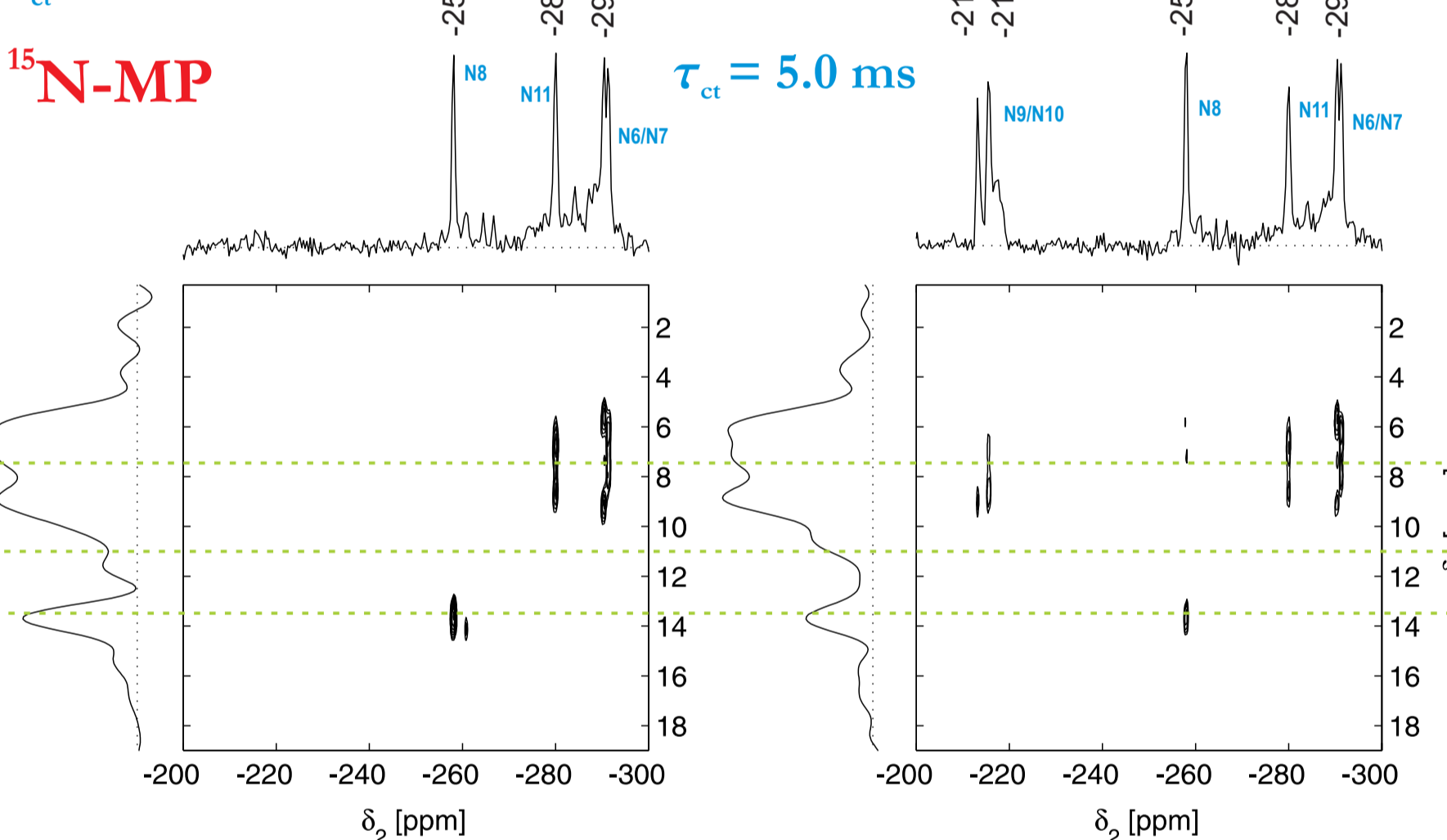
### <sup>1</sup>H-<sup>13</sup>C Correlation



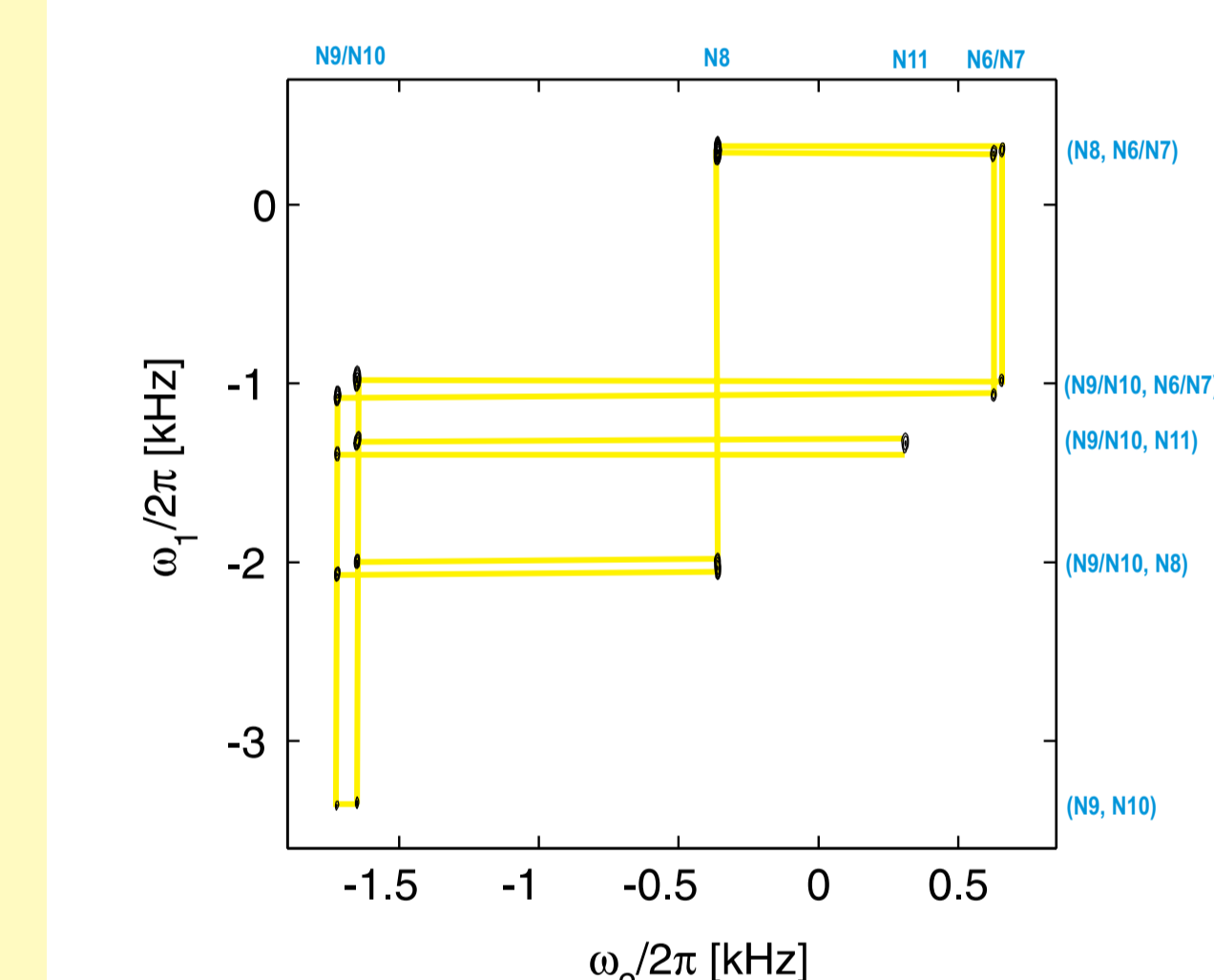
### <sup>1</sup>H-<sup>31</sup>P Correlation



### <sup>1</sup>H-<sup>15</sup>N Correlation



### <sup>15</sup>N-MP <sup>15</sup>N-<sup>15</sup>N Double-Quantum

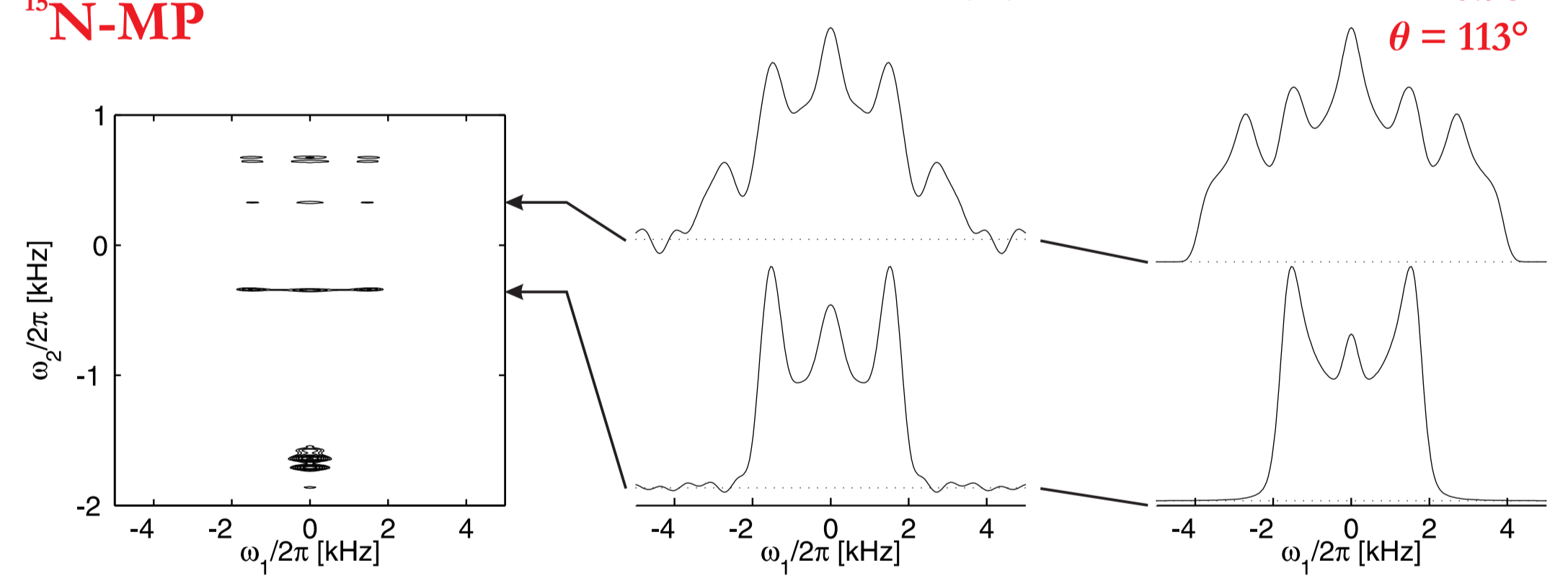


### <sup>1</sup>H-<sup>15</sup>N Distances

Two-dimensional chemical shift / heteronuclear dipolar coupling correlation spectrum of MP. The spectrum was obtained with a 2D constant-time sequence employing R182<sup>9</sup> as heteronuclear recoupling sequence [5]. The experiment was performed in an external field of 7.1 T and a spinning frequency of 20 kHz. The basic element was given by a single 180° pulse.

In addition average Hamiltonian simulations are shown, which show the key features of the dipolar lineshapes.

### <sup>1</sup>H-<sup>15</sup>N Distances

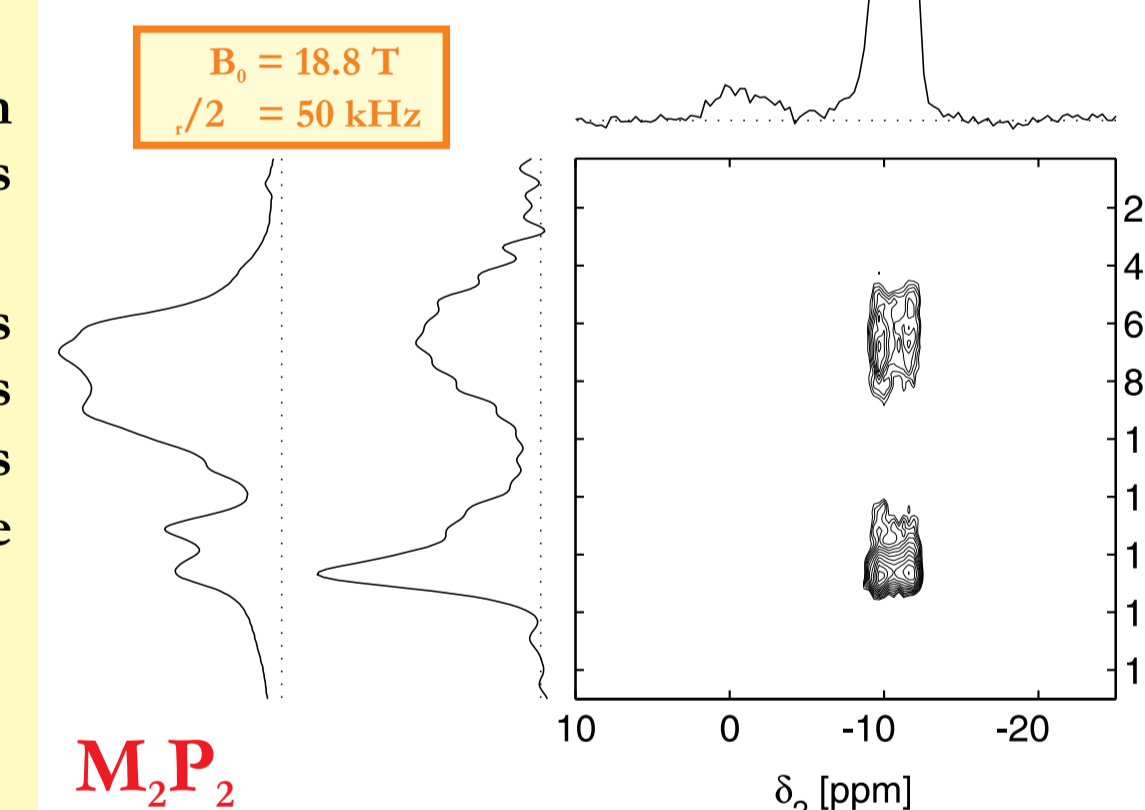


### M<sub>2</sub>P<sub>2</sub>: <sup>1</sup>H-<sup>31</sup>P Correlation:

On the right <sup>1</sup>H-<sup>31</sup>P heteronuclear correlation spectra for melamine pyrophosphate (M<sub>2</sub>P<sub>2</sub>) is shown.

The changes in the proton conformation is evident from the spectra. The resonances from one of the the <sup>1</sup>H attached to PO<sub>2</sub> groups disappear for the M<sub>2</sub>P<sub>2</sub> whilst the resonance stemming from the NH remains.

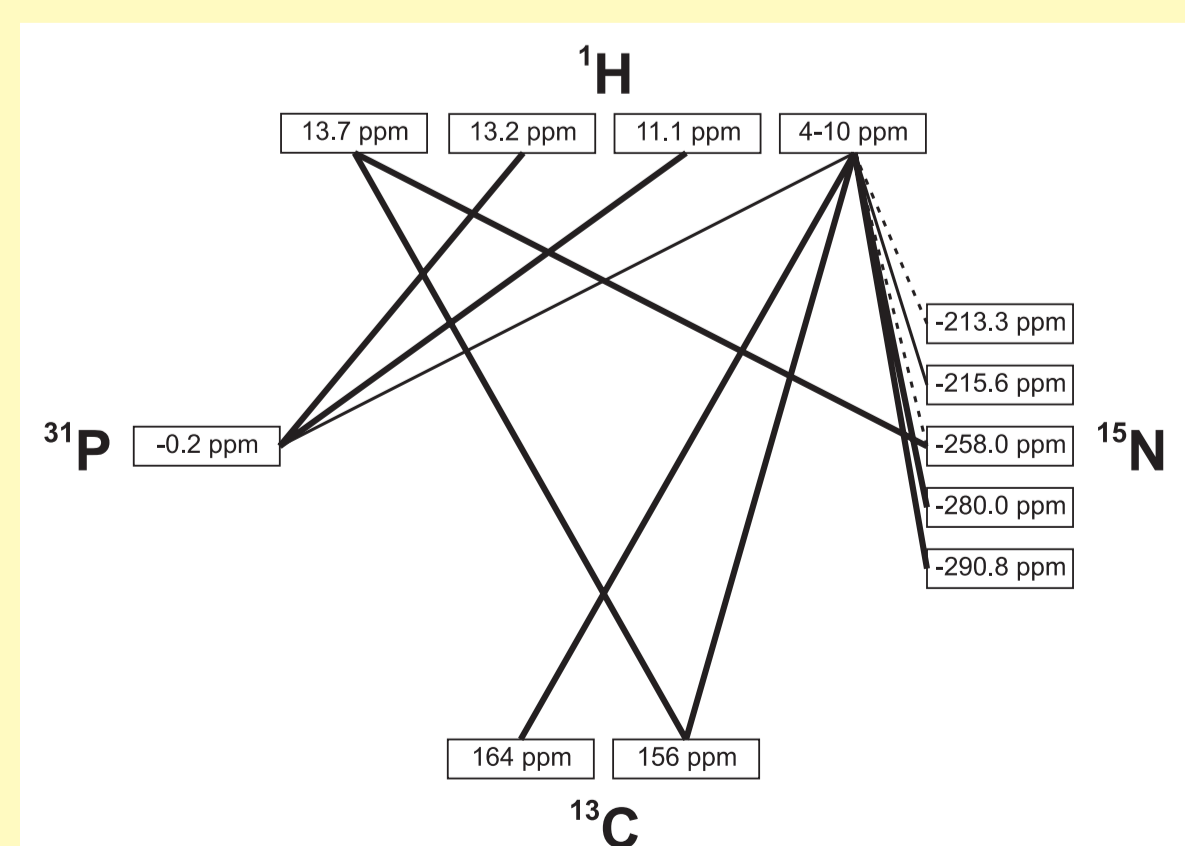
### <sup>1</sup>H-<sup>31</sup>P Correlation



## Discussion for MP

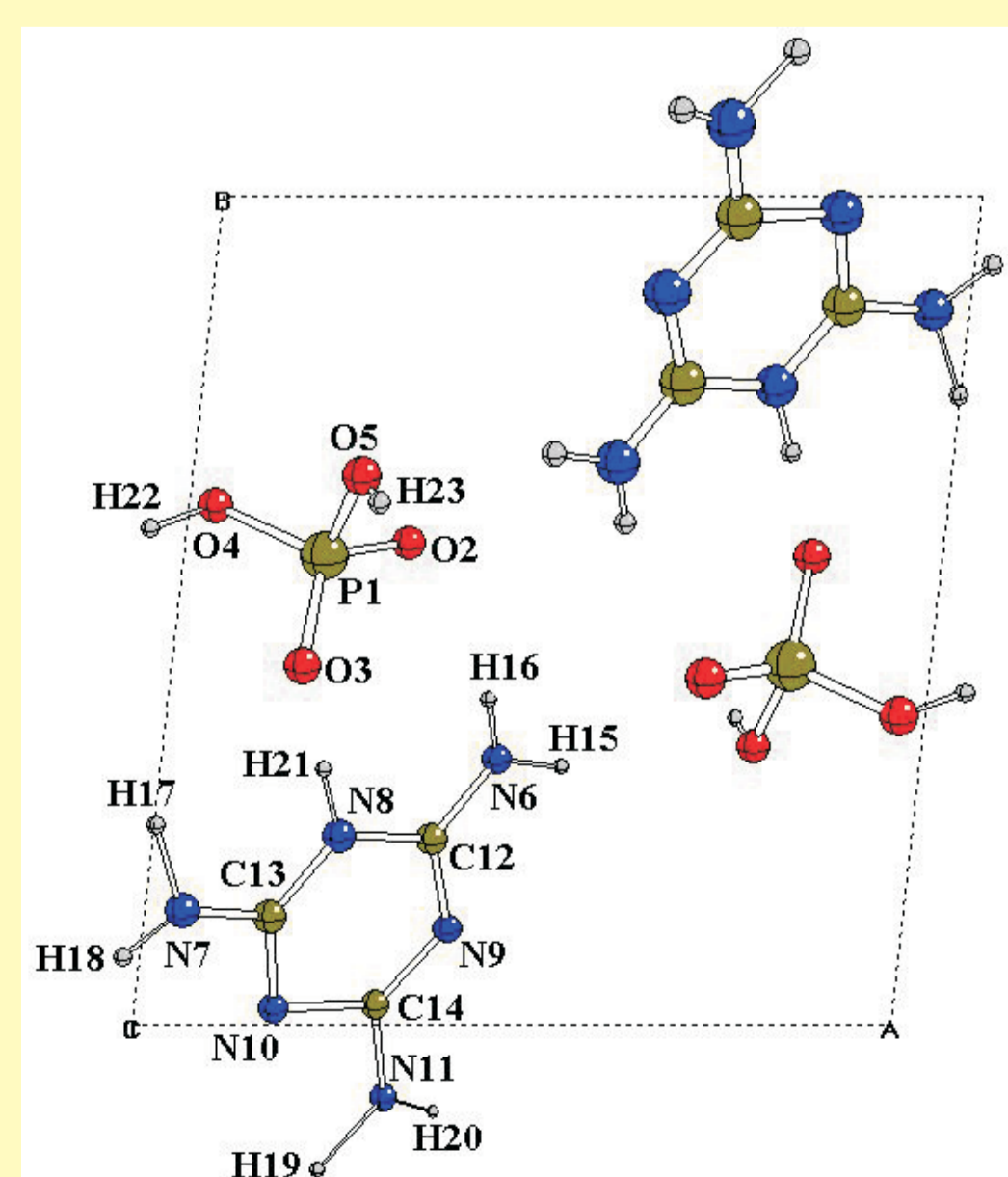
### MP Heteronuclear Correlations:

- <sup>1</sup>H with chemical shifts 13.2 and 11 ppm are attached to PO<sub>4</sub> groups.
- <sup>1</sup>H with chemical shift 13.2 ppm have a close contact to <sup>15</sup>N with shift -258.0 ppm (hydrogen bond).
- <sup>1</sup>H with shift 11 ppm have no close contact to spins in the melamine molecule.
- <sup>15</sup>N with chemical shifts -213.3 and -215.6 ppm are deprotonated.
- <sup>15</sup>N resonances at -280.0 and -290.8 ppm stem from NH and NH<sub>2</sub> groups in the melamine molecule which have <sup>1</sup>H shifts in the range 4-10 ppm.



### MP Unit Cell:

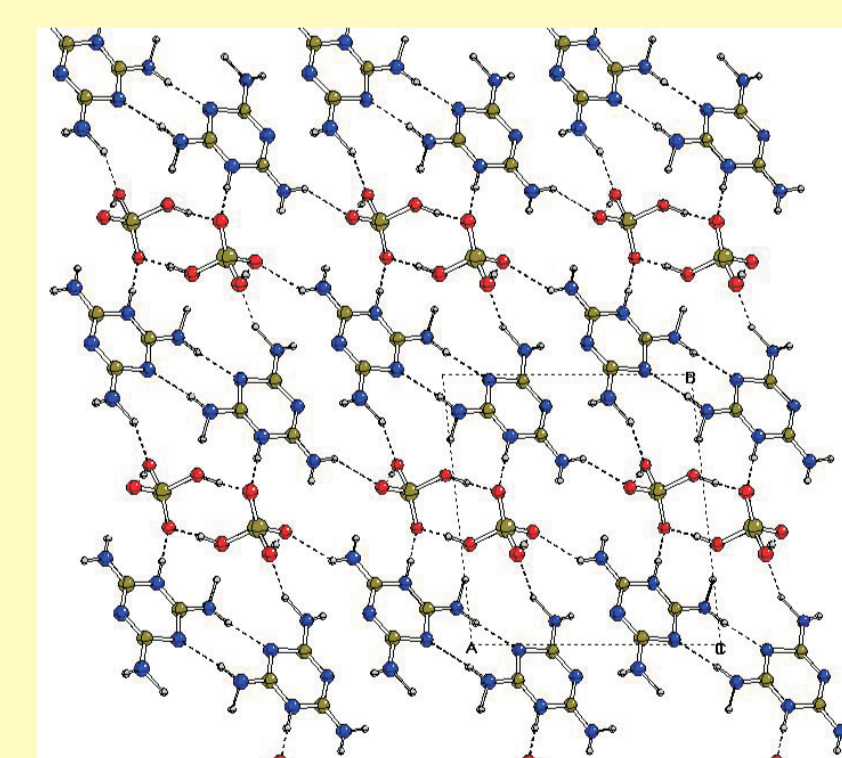
On the right the melamine phosphate unit is shown, including protons as proposed from the energetically favorable molecular modeling study and Rietveld refinement of the X-ray data. The NMR results are partly compatible with this model with a protonation of one of the ring nitrogens in the melamine.



### MP Crystal Structure:

The diagrams on the right show the crystal structure of MP including the protons. Some of the characteristics are:

- Layers of melamine molecules.
- Pairs of PO<sub>4</sub> groups.
- O-H...O inter and intra PO<sub>4</sub> groups hydrogen bonds.
- N-H...O hydrogen bonds between PO<sub>4</sub> groups and melamine molecules.
- Possible N-H...N hydrogen bonds between different melamine molecules.

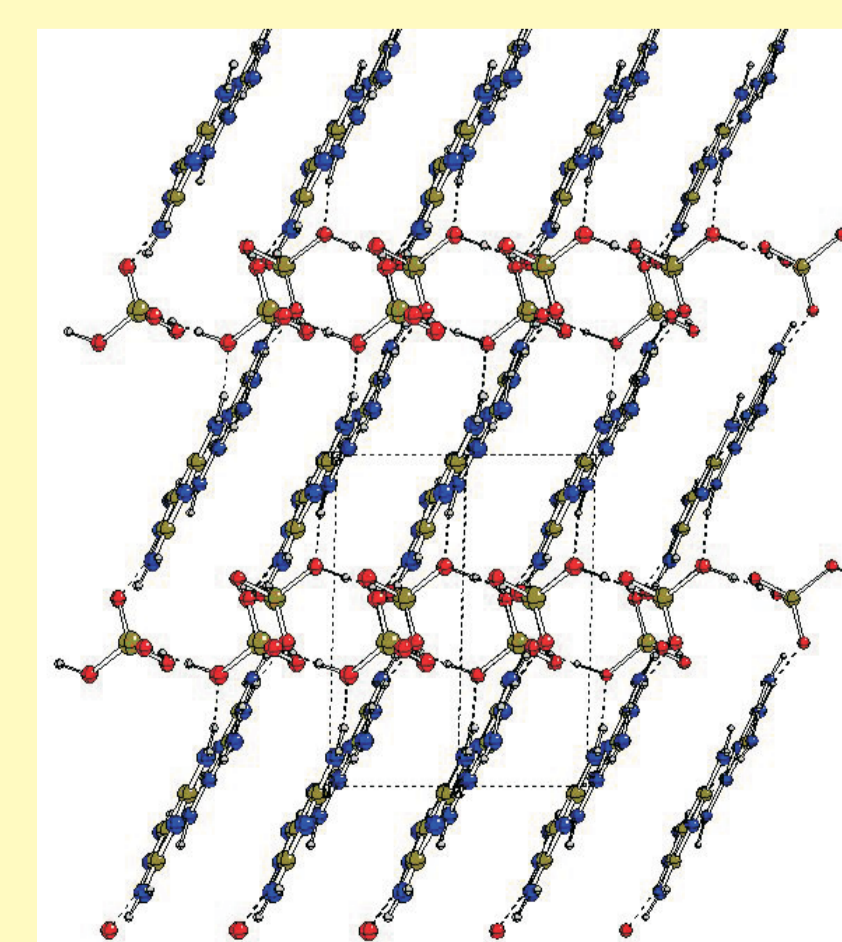


### Remaining Questions:

The 1D <sup>1</sup>H spectrum obtained at 18.8 T and 50 kHz spinning shows clearly a larger volume for the peak at 13.2 ppm compared to the peak at 11 ppm. This remains a contradiction to the proposed model for the proton positions, from which the opposite relationship is expected.

## Outlook

The solid-state NMR results presented here are still very qualitative. In a next step the existence of N-H...N hydrogen bonds should be shown experimentally by determining the <sup>15</sup>N-<sup>15</sup>N J-couplings over the hydrogen bonds.



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