

Supporting Information

Dynamics of water molecules and sodium ions in solid hydrates of nucleotides

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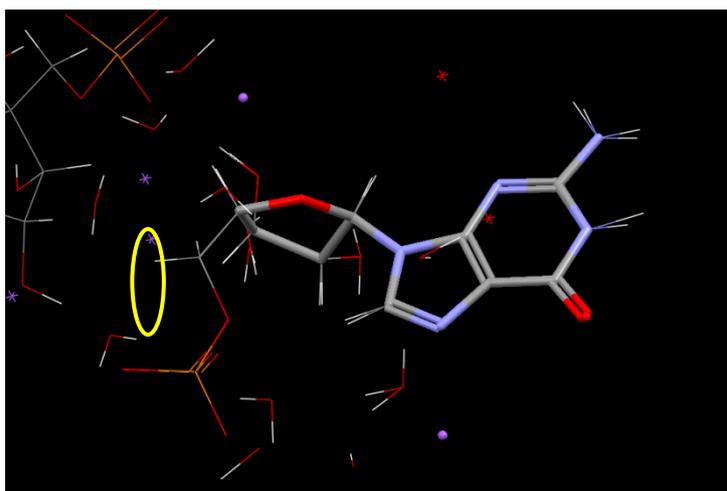


Figure S1. Overlay of GmP structures GUOPNA10 and GUOPNA11. The most important difference is highlighted by the yellow circle.

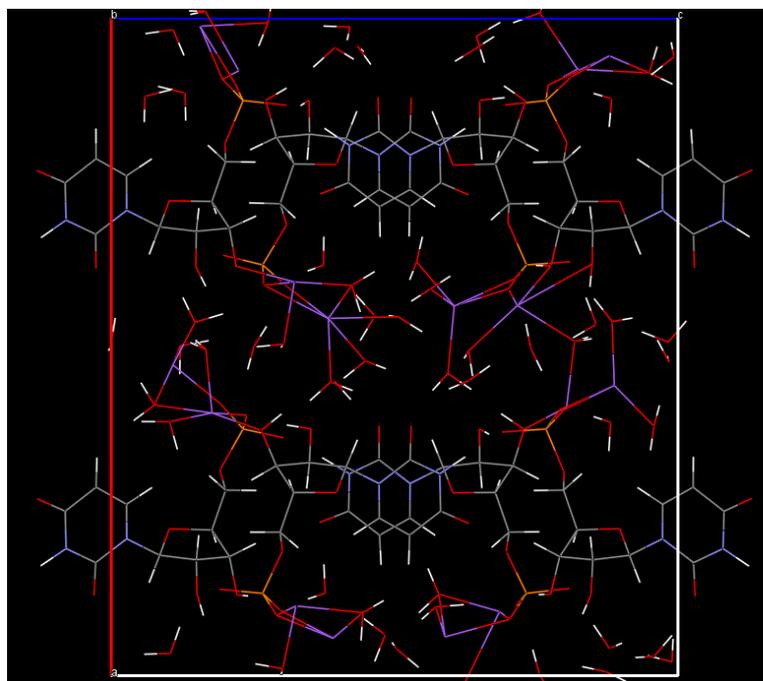


Figure S2. Optimised structure of UMP – starting point for the MD simulation.

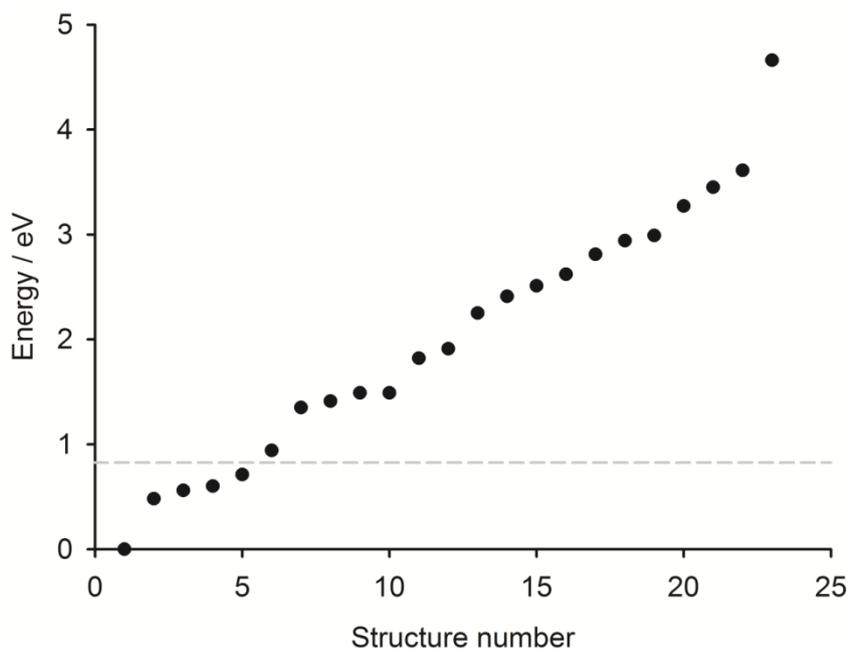


Figure S3. Relative energies of the 23 relaxed geometry snapshots from the MD simulation of UMP.

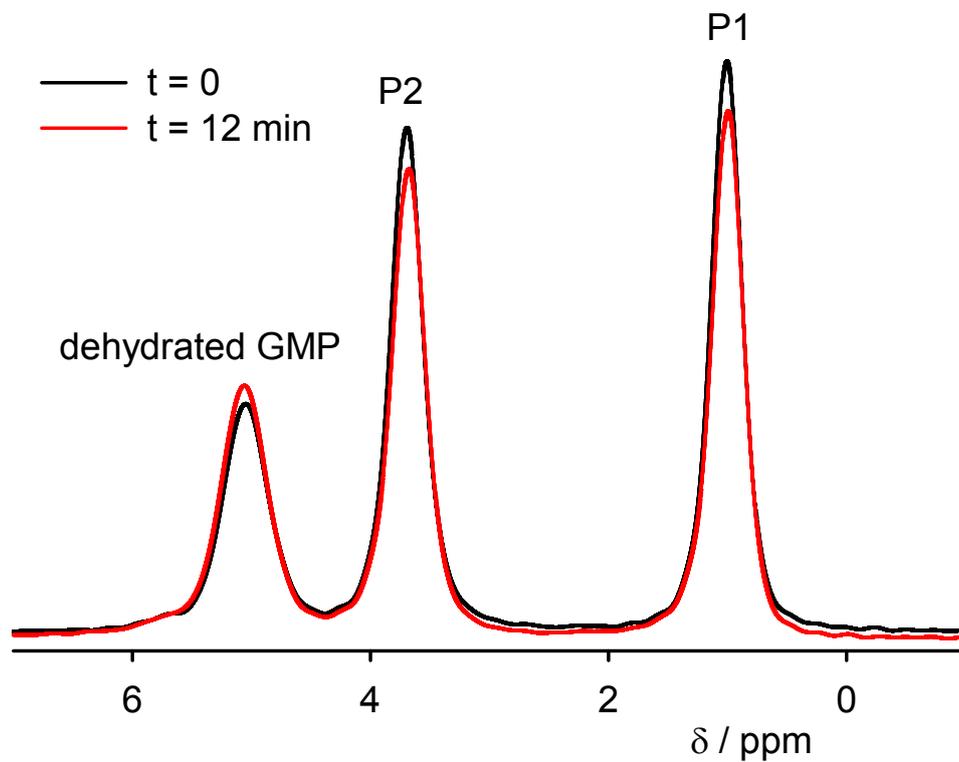


Figure S4. ^{31}P NMR spectra of GMP acquired at 40 °C. The intensity of the two GMP signals steadily decreases while the intensity of the signal of the dehydrated form increases.

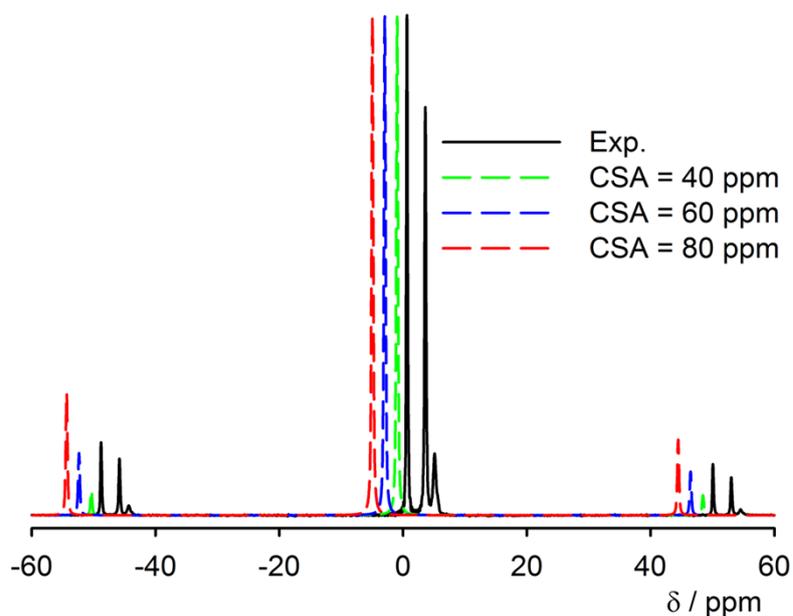


Figure S5. Comparison of experimental ^{31}P CP-MAS spectrum of GMP with simulated spectra with different values of the CSA anisotropy parameter (asymmetry fixed at zero). The ratio of sideband intensities is a significantly better matched with the value of 60 ppm (± 10 ppm one-standard-deviation error bar) obtained from fitting.

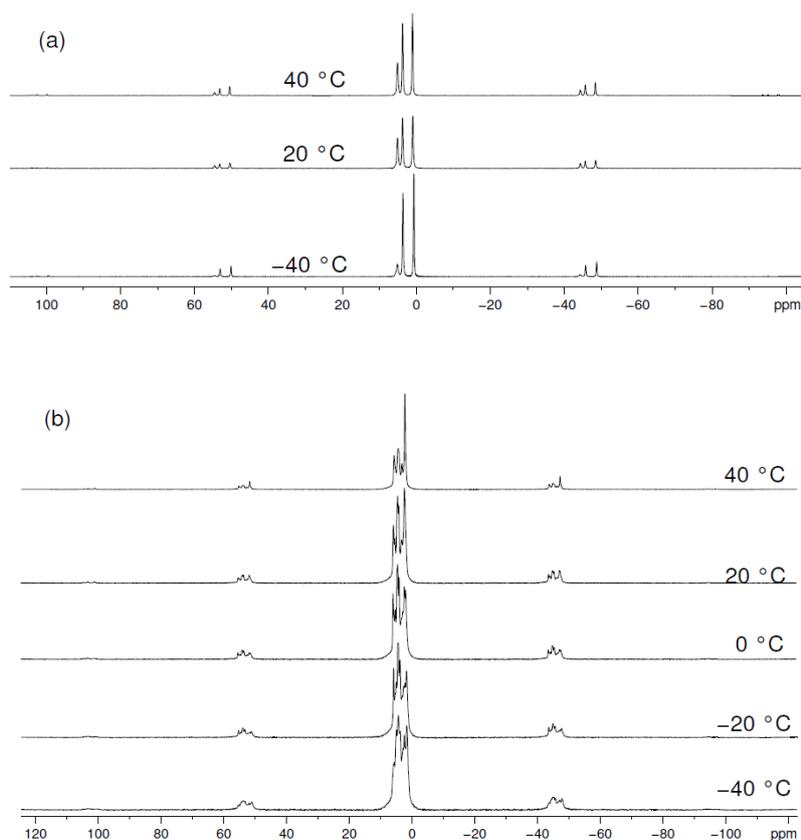


Figure S6. Variable temperature ^{31}P NMR spectra of (a) GMP and (b) UMP.

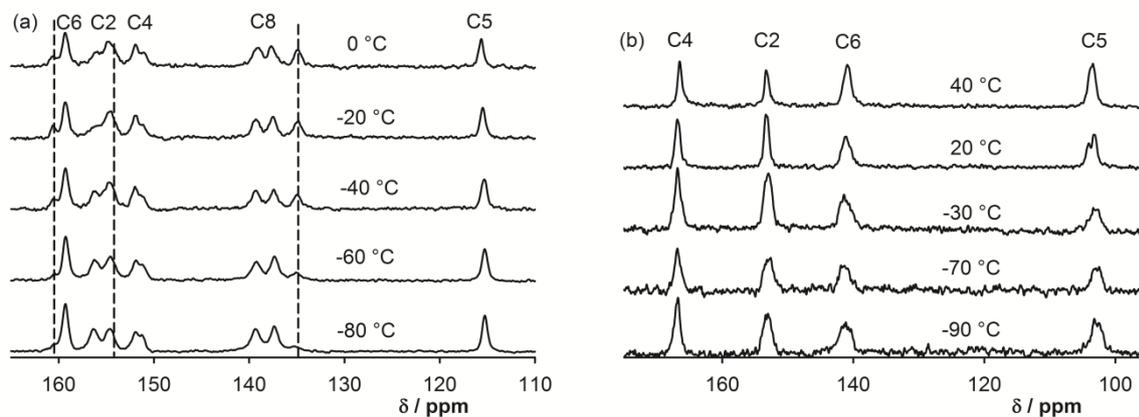


Figure S7. Variable temperature ^{13}C CP-MAS spectra (aromatic region) of (a) GMP (dashed lines indicate peaks associated with the dehydrated form) and (b) UMP. See Figure 1 for atom numbering.

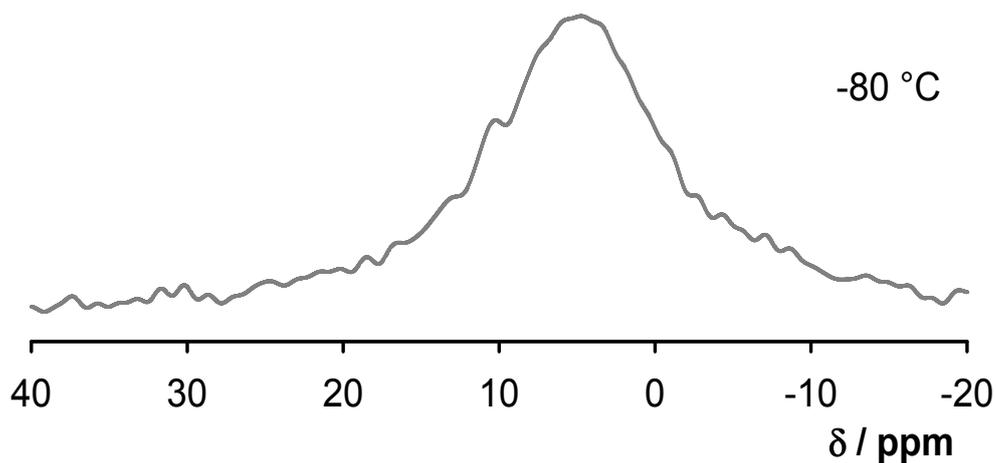


Figure S8. Expansion of the central line of ^2H MAS spectrum of UMP. The feature at 10 ppm, while close to the noise level, is observed consistently in other sidebands and spectra obtained at different temperature, and is probably associated with the NH hydrogen.

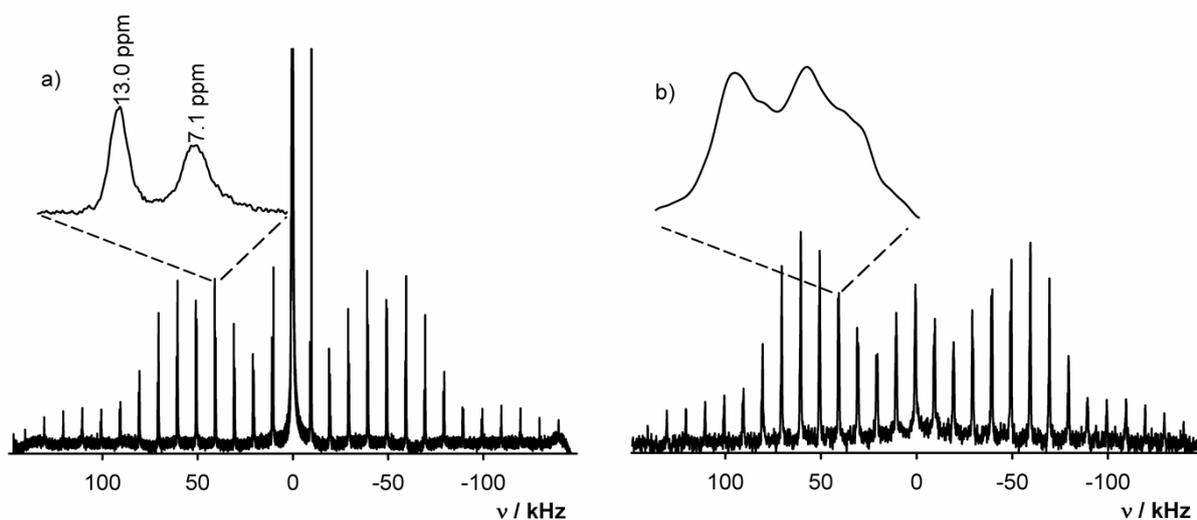


Figure S9. Experimental ²H MAS spectra (MAS rate 10 kHz) of GMP at r.t.: (a) a fresh sample and (b) of a sample left at r.t. for one month.

The ²H MAS spectra of GMP recrystallized from D₂O/CH₃CH₂OD, shown in Fig. S8, present some puzzling features. The spectrum of the fresh sample, (a), has a strong (truncated) signal at the central band corresponding to residual deuterated solvent, but there are also sharp, and notably asymmetrical side ± 1 sidebands associated with this resonance; these are most likely to be artefacts associated with the high dynamic range. The shift values shown are therefore extracted from one of the third order sidebands. It is difficult to assign these peaks due to the number of exchangeable hydrogens involved. Estimating the chemical shifts, δ , from the CASTEP-predicted shieldings, σ (using $\delta = 30.7 \text{ ppm} - \sigma$), these are: $7 \times \text{H}_2\text{O} + 2 \times \text{ribose-OH}$ (7.7 ppm), NH₂ (5.7 and 11.2 ppm), guanine-NH (13.7 ppm). In the aged sample, (b), the residual D₂O has gone, but additional resonances have appeared, which strongly suggest that the sample has degraded. It is not obvious from these spectra where the signal from the structural D₂O, which is expected to dominate, appears. It is very unlikely to be included in the sharp signal in (a), since the material in (b) is only partially transformed and so should still contain D₂O. One plausible explanation is that the structural D₂O signals are motionally broadened at ambient temperature by C2 flip motions. Unfortunately it was not possible to explore this further due to the sample degradation and the difficulty of preparing fresh sample.

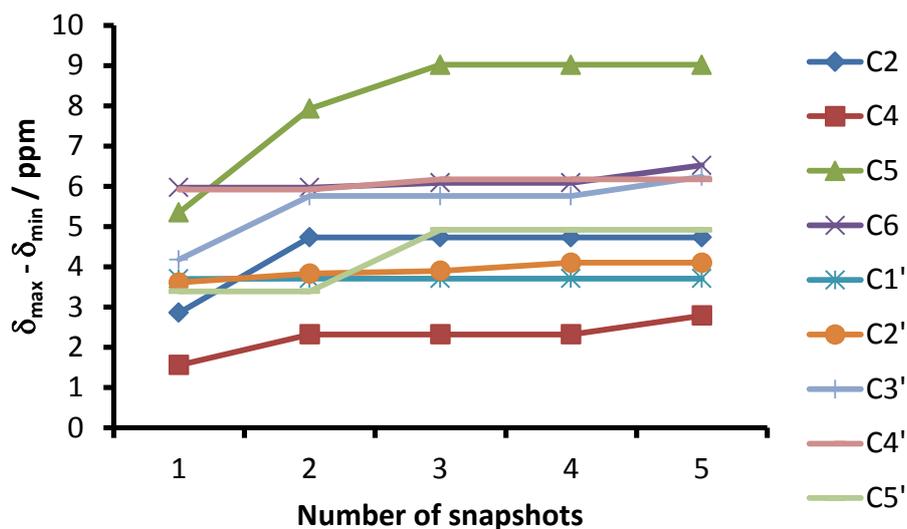


Figure S10. The convergence of calculated spans of ^{13}C chemical shifts with the number of MD snapshots.

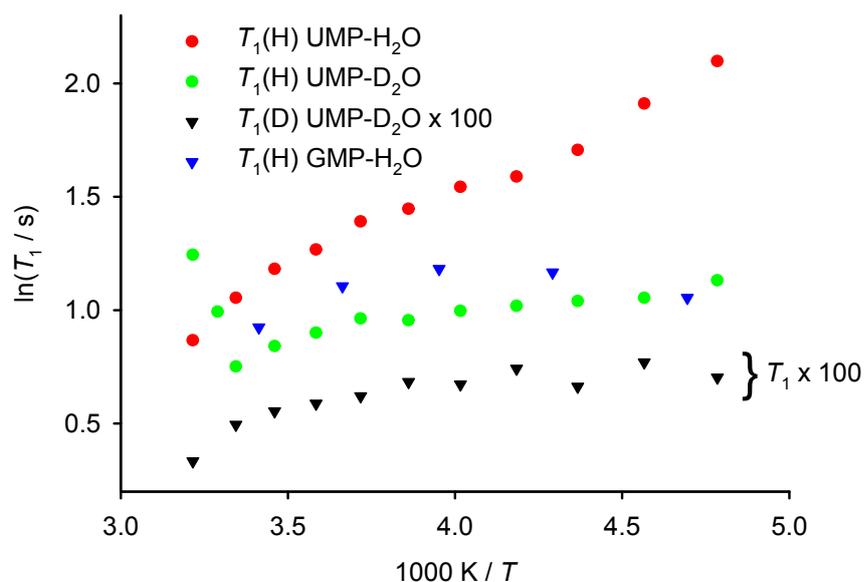


Figure S11. Temperature dependence of ^1H and ^2H relaxation times T_1 of UMP samples recrystallized from H_2O and D_2O , and GMP sample recrystallized from H_2O . Estimated statistical errors are of the order of the size of the symbols.

Fig. S11 shows the temperature dependence of ^1H and ^2H spin-lattice relaxation times in UMP- H_2O , UMP- D_2O and GMP- H_2O (it was not possible to measure relaxation times in GMP- D_2O due to the limited amount of sample and sample degradation). Interpretation of the results is complicated by multiple factors:¹⁻² for example, rapid spin-diffusion means that only an effective ^1H relaxation rate is observed for the ^1H sites. The ^2H relaxation is, in principle, more site-specific, but the UMP- D_2O spectrum shows only a single resonance, implying that, at the least, the water and ribose-OH signals are in rapid chemical exchange (as they are mutually involved in hydrogen-bonding). Depending on

the timescale of the exchange processes, the ^2H relaxation rates will also be affected by chemical exchange as well as dynamics of the D_2O molecules themselves. As a result, only limited conclusions can be drawn from this data.

^1H spin-lattice relaxation times in the UMP- H_2O sample are significantly temperature dependent with T_1 values going from 8.2 s at $-80\text{ }^\circ\text{C}$ to 2.4 s at $22\text{ }^\circ\text{C}$ (see figure above), but the corresponding relaxation times in the UMP- D_2O sample are shorter (2–4 s) and almost temperature independent over the observed temperature range. One possible explanation for the shorter proton relaxation times in UMP- D_2O compared to UMP- H_2O is that the proton relaxation in this sample is being assisted by cross-relaxation with the rapidly relaxing deuterium nuclei; the ^1H and ^2H relaxation curves track each other and cross-relaxation and NOE effects are frequently observed for the $^{13}\text{C}/^1\text{H}$ pair e.g. in methyl groups. A weakness of this explanation is that the ^1H relaxation is also relatively fast in GMP- H_2O , where the water is not expected to be dynamic. An alternative explanation is that the relaxation rate of the water ^1H is intrinsically long (as is generally the case in pure water, due to very rapid re-orientational tumbling) and that the overall ^1H relaxation rates in UMP- H_2O are long as a result, and the shorter relaxation rate of UMP- D_2O reflects relatively fast relaxation of the non-water protons. A priori, however, ^1H relaxation of the GMP protons is not expected to be fast, given the lack of methyl groups to drive relaxation. The fact that such different rationalisations can be given for the same data illustrates the difficulties referred to above.

The deuterium T_1 relaxation times (available for UMP- D_2O only) are somewhat less ambiguous. They are very short (7–11 ms) and only modestly temperature dependent. These values can be compared to the minimum value of T_1 of about 3 ms calculated for a deuterium quadrupole coupling of 200 kHz and 77 MHz ^2H Larmor frequency using an isotropic diffusional re-orientation model.³ The jump rates here must be of the order of 10^8 to 10^{10} s. Models involving more limited re-orientation, such as C_2 symmetry or tetrahedral jumps, would further reduce the range of jump frequencies that are compatible with these short relaxation times.⁴ The fact that the deuterium T_1 relaxation rate is fast, but relatively temperature independent is compatible with the existence of multiple sites with a distribution of effective barrier heights, although it should be pointed out that the ^1H relaxation of the GMP sample (where such complex dynamics is not expected) shows very similar behaviour! Note that although the ^1H and ^2H spin-lattice relaxation will be sensitive to the same dynamic processes, the relaxation mechanisms involved are quite different (largely dipolar and largely quadrupolar respectively), and there is a significant difference (a factor of ~ 6.5) in the Larmor frequencies involved. The correlation functions for the dynamics will be complex and so quantitative interpretation of the relaxation data, which can be highly informative for better-defined systems,⁴ would be very difficult.

Table S1. Ranges of ^{31}P isotropic shielding for the five optimised geometries of UMP.

Snapshot	$\sigma^{31\text{P}}_{\text{min}} / \text{ppm}$	$\sigma^{31\text{P}}_{\text{max}} / \text{ppm}$	$\Delta\sigma / \text{ppm}$
2.8 ps	267.7	278.9	11.2
3.6 ps	269.3	276.3	7.0
3.8 ps	266.8	278.1	11.3
4.2 ps	267.7	276.3	8.6
4.6 ps	267.6	279.5	12.9

Elemental analyses of the UMP system recrystallized from H_2O -MeOH (2:1), H_2O -MeOH (1:1), and H_2O -EtOH (2:1).



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ELEMENTÁRNÍ ANALÝZA - ELEMENTAL ANALYSIS

Vzorek / Sample: UMP-Na₂ II.	Jméno / Name: Šála
Stanovované prvky / Elements to be analyzed: C H N	Teoretické složení / Theoretical composition (%): C 21,87 H 5,10 N 5,67
Číslo analýzy / Analysis number: 13960	Datum / Date: 4.5.2012

Automatická CHN analýza / Automatic CHN analysis

Navážka / Sample amount (mg)	% C	% H	% N
1 1,680	22,07	5,08	5,51
2			
3			
4			



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ELEMENTÁRNÍ ANALÝZA - ELEMENTAL ANALYSIS

Vzorek / Sample: UMP-Na₂ III.	Jméno / Name: Šála
Stanovované prvky / Elements to be analyzed: C H N	Teoretické složení / Theoretical composition (%): C 21,87 H 5,10 N 5,67
Číslo analýzy / Analysis number: 13961	Datum / Date: 4.5.2012

Automatická CHN analýza / Automatic CHN analysis

Navážka / Sample amount (mg)	% C	% H	% N
1 2,341	22,01	4,74	5,54
2			
3			
4			



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ELEMENTÁRNÍ ANALÝZA - ELEMENTAL ANALYSIS

Vzorek / Sample: UMP-Na₂ IV.	Jméno / Name: Šála
Stanovované prvky / Elements to be analyzed: C H N	Teoretické složení / Theoretical composition (%): C 21,87 H 5,10 N 5,67
Číslo analýzy / Analysis number: 13962	Datum / Date: 4.5.2012

Automatická CHN analýza / Automatic CHN analysis

Navážka / Sample amount (mg)	% C	% H	% N
1 1,967	22,40	5,12	5,54
2			
3			
4			

References

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2. Belton, P. S., *Magn. Reson. Chem.*, 2011, **49**, S127-S132.

3. Vold, R. R., Deuterium NMR studies of dynamics in solids and liquid crystals. In *Nuclear Magnetic Resonance Probes of Molecular Dynamics*, Tycko, R., Ed. Kluwer Academic Publishers: Dordrecht, 1994; pp 27-112.
4. Apperley, D. C.; Markwell, A. F.; Frantsuzov, I.; Illott, A. J.; Harris, R. K.; Hodgkinson, P., *Phys. Chem. Chem. Phys.*, 2013, **15**, 6422-6430.