

Suppression of isotopic polymorphism

SUPPLEMENTARY INFORMATION

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1 Crystal structure refinement statistics

Table S1: Single crystal refinement statistics for all structures

Pressure / GPa	0.0	0.21	0.57	1.47
X-ray wavelength / Å	0.6889	0.6889	0.6889	0.6889
Chemical formula	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅
Formula weight / g mol ⁻¹	335.44	335.44	335.44	335.44
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> -axis / Å	7.39400(3)	7.39220(3)	7.30140(3)	7.17450(3)
<i>b</i> -axis / Å	8.93630(7)	8.92720(8)	8.70170(7)	8.43780(7)
<i>c</i> -axis / Å	13.68800(6)	13.65240(9)	13.23390(7)	12.73460(7)
α / °	100.541(11)	100.317(14)	100.090(11)	100.591(12)
β / °	118.408(7)	118.354(9)	117.346(7)	115.749(7)
γ / °	103.460(8)	103.641(9)	104.142(8)	104.468(8)
Volume / Å ³	726.65(10)	724.49(12)	682.70(9)	633.45(9)
Density / gcm ⁻³	1.643	1.648	1.749	1.885
Parameters	77	77	77	77
No. independent reflections	494	620	555	646
<i>R</i> 1, <i>wR</i> (<i>I</i> > 2σ)	0.237, 0.552	0.139, 0.389	0.119, 0.406	0.102, 0.246
Goodness of fit	1.6344	1.7140	1.9981	1.0080
μ / cm ⁻¹	0.890	0.893	0.948	1.021
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	-0.60, 0.60	-0.55, 0.63	-0.56, 0.49	-0.48, 0.56
Completeness, resolution / Å	23.93%, 0.90	29.76%, 0.90	28.48%, 0.90	20.79%, 0.75

Table S2: Single crystal refinement statistics for all structures (continued)

Pressure / GPa	2.86	3.75	4.57
X-ray wavelength / Å	0.6889	0.6889	0.6889
Chemical formula	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅
Formula weight / g mol ⁻¹	335.44	335.44	335.44
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> -axis / Å	7.09540(3)	7.04560(3)	7.02900(3)
<i>b</i> -axis / Å	8.23750(7)	8.17400(7)	8.00850(6)
<i>c</i> -axis / Å	12.39660(6)	12.21220(6)	12.08050(6)
α / °	100.861(11)	101.337(11)	101.110(10)
β / °	114.958(7)	114.199(7)	114.232(7)
γ / °	104.500(8)	104.453(8)	104.203(8)
Volume / Å ³	599.22(8)	584.57	567.09(7)
Density / gcm ⁻³	1.992	2.042	2.105
Parameters	77	77	77
No. independent reflections	548	525	669
<i>R</i> 1, <i>wR</i> (<i>I</i> > 2σ)	0.118, 0.385	0.117, 0.390	0.135, 0.424
Goodness of fit	1.8296	1.9401	1.9834
μ / cm ⁻¹	1.080	1.107	1.141
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	-0.64, 0.74	-0.79, 0.89	-1.11, 1.07
Completeness, resolution / Å	22.84%, 0.80	22.54%, 0.80	24.48%, 0.76

Table S3: Single crystal refinement statistics for all structures (continued)

Pressure/temperature	0.4 GPa	150 K	80 K
X-ray wavelength / Å	0.5159	1.5406	1.5406
Chemical formula	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅	C ₁₀ H ₈ N ₁ O ₁ Cl ₅
Formula weight / g mol ⁻¹	335.44	335.44	335.44
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>Cc</i>	<i>Cc</i>
<i>a</i> -axis / Å	3.8385(8)	3.86184(17)	3.8299(3)
<i>b</i> -axis / Å	27.440(6)	27.5870(14)	27.5220(19)
<i>c</i> -axis / Å	12.924(5)	13.0065(5)	13.0115(16)
β / °	95.52(3)	95.678(4)	95.766(10)
Volume / Å ³	1355.0(5)	1378.87(11)	1364.6(2)
Density / gcm ⁻³	1.762	1.731	1.750
Parameters	102	173	275
No. independent reflections	1062	2082	2035
<i>R</i> 1, <i>wR</i> (<i>I</i> > 2σ)	0.062, 0.124	0.048, 0.121	0.060, 0.153
Goodness of fit	0.9871	0.9623	1.0078
μ / cm ⁻¹	0.423	9.504	9.603
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ / e Å ⁻³	-1.21, 1.02	-0.39, 0.73	-0.33, 0.49
Completeness, resolution / Å	63.44%, 0.92	97.77%, 0.81	96.54%, 0.80

2 Low-temperature neutron diffraction

In an effort to grow the as-yet-unobtained TD form of MPPCP, we carried out low-temperature neutron diffraction on the POLARIS instrument at the ISIS Neutron and Muon Facility, aiming to observe crystallisation from solution *in situ*. The choice of neutron radiation would have allowed more decisive determination of whether the phenol group was protonated or deuterated. Although it is believed the isotope of only the phenolic hydrogen is influential in determining the final crystal form, we opted to use perdeuterated methylpyridine to avoid any possibility of H/D exchange, as well as negating the issue of incoherent scattering of neutrons by hydrogen. Numerous instances of MPPCP-d₈ were measured, covering a temperature range of 183–250 K. Samples were either loaded at room temperature or were rapidly transferred to a cryostat following immersion in liquid nitrogen. In nearly all cases, we only observed growth of the MD form—however, this does indicate that there is unlikely to be any residual hydrogenous impurity in our sample. The conditions we now describe led to the lone observation we made of a signature reflection of the TD form.

Methylpyridine-d₇ was purchased from QMX Laboratories and used as supplied. Pentachlorophenol-h₁ was purchased from Sigma Aldrich and was subjected to repeated cycles of being stirred with D₂O and filtration, leading to the formation of pentachlorophenol-d₁. 0.297 g of MP-d₇ was mixed with 0.757 g of PCP-d₁ and this was dissolved in 1.2 mL of MeOD-d₄. The resulting solution was sealed in a 6 mm vanadium can, which was immersed in liquid nitrogen. The can was rapidly transferred to a cryostat set at 183 K, in the POLARIS instrument.

The sample was held at 183 K, where no crystallisation was observed. The presence of a single, broad peak in the diffraction data at ca. 3.5 Å indicated the possible formation of either an amorphous form, or significant ordering of the MP and PCP molecules in solution. The can was then slowly warmed to try and induce crystallisation (which occurs readily at ambient temperature). On reaching 215 K, formation of small peaks at low *d*-spacing were observed and the temperature ramp was halted, such that temperature slowly drifted upward to 217 K. Data were collected over 30 minute intervals, in order to gain sufficient statistics to identify peaks. A stackplot of the measurements during this period are shown in Figure S2.

A single peak attributable to TD was observed after ca. 2.5 hours—this is identified with the red arrow in Figure S2. There are unconvincing traces of this peak on the patterns either side of that coloured red, and is clearly not present across all other patterns. All other peaks are indicative of the MD form—this has been established unambiguously from other sample loadings that led to more complete crystallisation. Figure S3 shows approximate fits to the data for the MD and TD forms, using Topas Academic. The data are not of sufficient quality to allow any form of robust refinement, so we have done the following: i) imported the known cell and atomic coordinates of the MD and TH forms, ii) substituted H for D in the TH structure, and iii) allowed only a scale factor to refine for each sample, as well as 13 background terms which approximately describe its oscillating form. The unit cell parameters and peak shape could not be refined stably, so these were held fixed—hence there is some obvious mismatch in peak positions. Though the ‘fit’ is crude, it is clear that the MD form cannot account for the peak at 8 Å—there are no predicted reflections in its vicinity. The TD form can account for this reflection—significantly, this corresponds to the most intense peak in the calculated TD pattern.

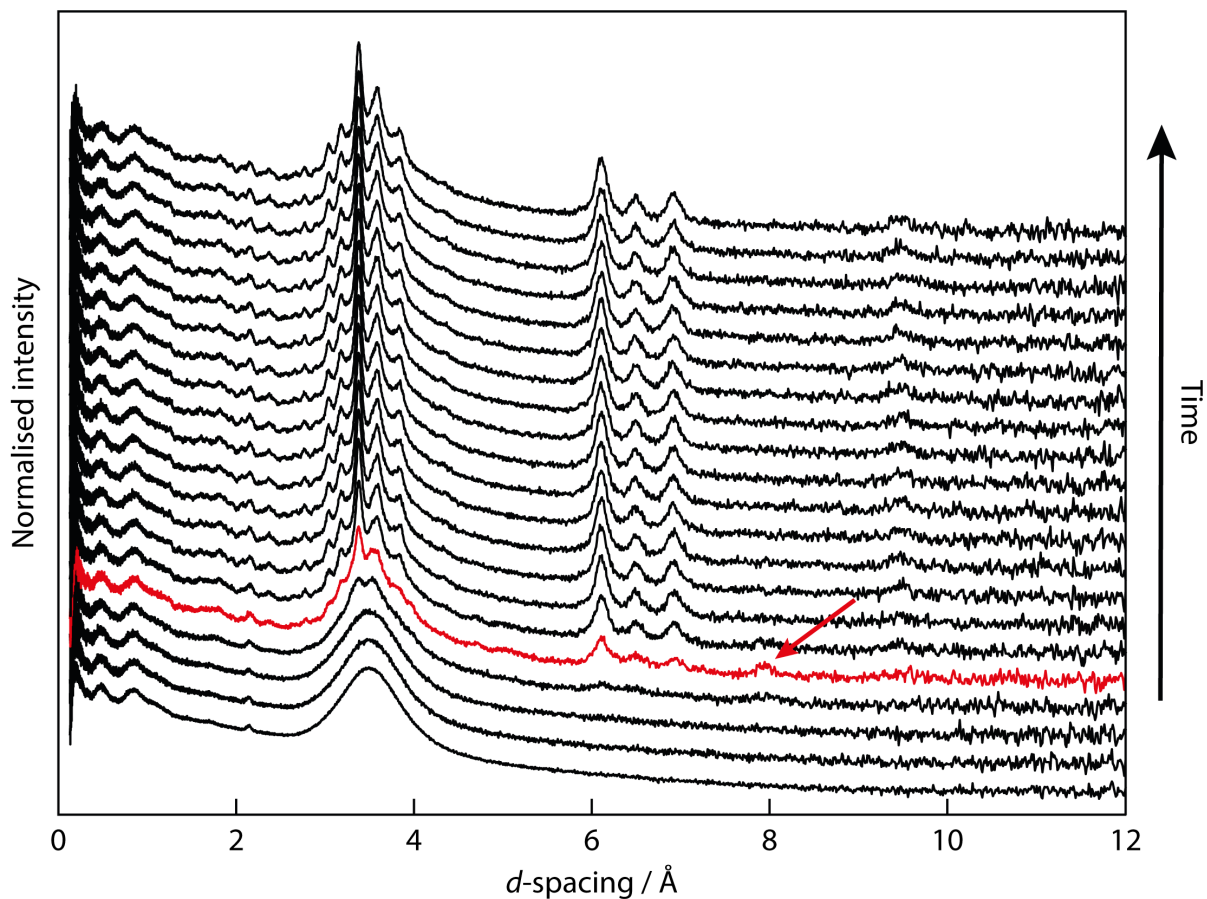


Figure S1: POLARIS powder diffraction patterns of MPPCP-d₈. Each pattern represents 30 minutes of collection time, with progression being shown from bottom to top. The temperature is 215 K for the earliest pattern, and this increases to ca. 217 K after 2 hours. The pattern coloured red shows the only significant observation of a peak at 8 Å, indicated by the red arrow—the peak is greatly diminished 30 minutes later, and entirely absent another 30 minutes later.

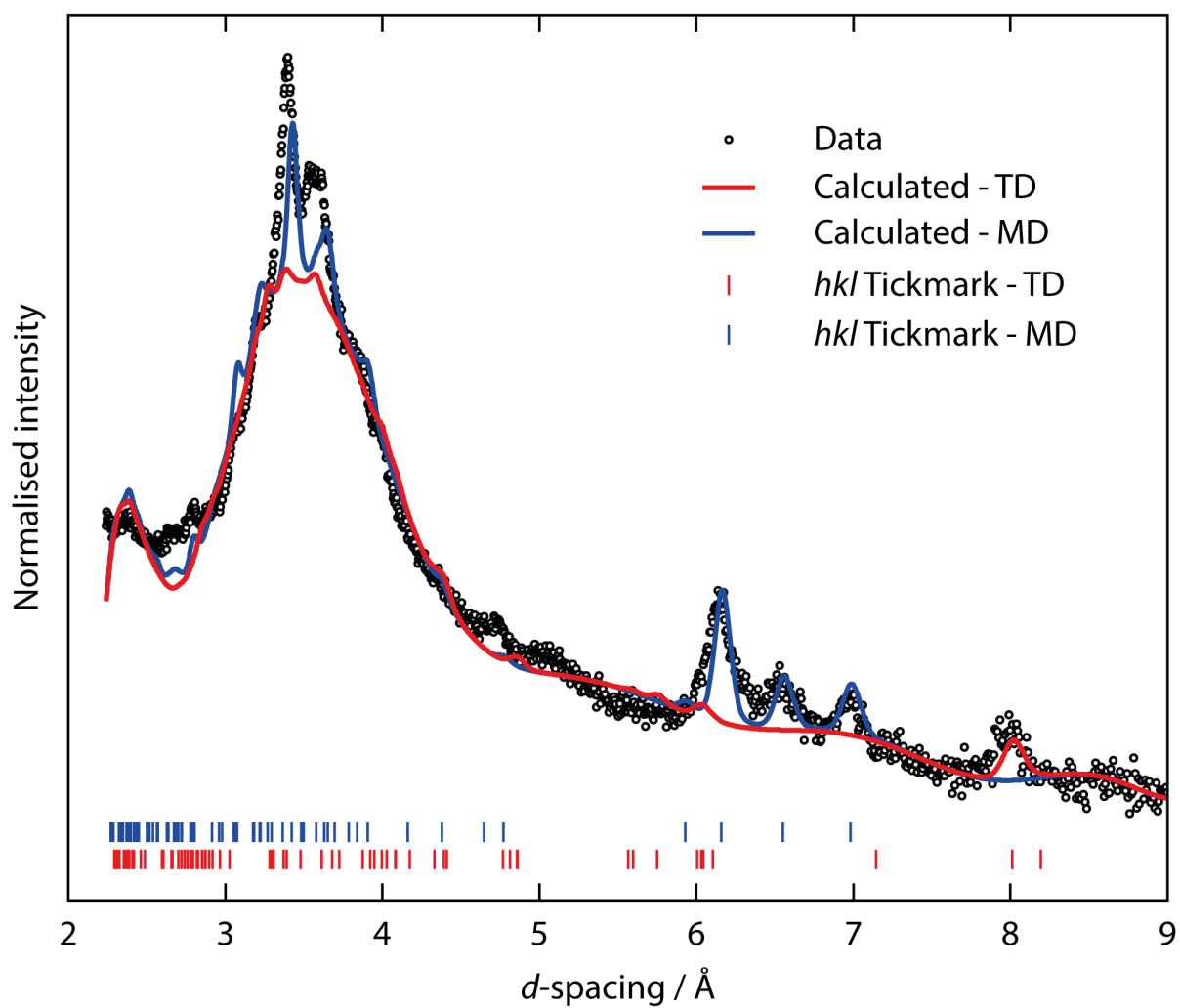


Figure S2: Calculated MD and TD structures. A scale factor and background parameters have been allowed to refine for each structure. The fit and tickmarks for the MD structure are shown in blue, and TD in red. Only the TD structure can account for the peak at 8 Å.