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Adenine phase transformations in situ: crystalline, non-crystalline and in between

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The first crystal structure of a nucleobase was solved in 1954. It was uracil that got the investigations started, and by 1970 three structures of three other nucleobases were determined.
However, the initially published structure of uracil turned out to be slightly wrong (1967). Anhydrous guanine was challenging to crystallize, and its structure was not determined until 2006. And adenine was no better – it did not crystallize until 2008, when Mahapatra and co-workers obtained single crystals of adenine via sublimation. The monoclinic layered structure with two molecules of adenine in the asymmetric unit was finally revealed, and the story seemed to have come to a happy end [1]. However, one question remained open - why was it so difficult?

Almost a decade later, investigations of commercial batches of adenine gave the better insight into the answer. Adenine prefers to crystallize as a mixture of two phases, where the monoclinic phase (polymorph I) is the minor phase. In our recent study, we have established procedures for selective preparation of both phases, and characterized polymorph II [2]. As expected, the new polymorph also featured a layered structure, but this time in an orthorhombic symmetry, with Z' = 1. What came as a surprise is that the new polymorph II is thermodynamically less stable at ambient conditions. But, is this also true at higher temperatures?

Our current interest is focused on the temperature-resolved investigations of adenine transformations. The experimental setup is based on a laboratory diffractometer, optimized to collect a complete X-ray diffraction pattern (74° in 2θ) in only two steps. Starting with polymorph I at room temperature, heating of the sample causes seemingly gradual transition to polymorph II. This behaviour makes the modelling of polymorph I structure increasingly difficult - patterns collected at higher temperatures can be almost equally well described with the crystal structures of I and II. Above 300°C abrupt change occurs, where the patterns are characterised by only one peak. This corresponds to a third polymorph (polymorph III) with a disordered layered structure, having an interlayer distance similar as in polymorphs I and II. This somewhat surprising liquid crystal state of polymorph III is accompanied with yet another unusual feature: XRPD patterns indicate negative thermal expansion (NTE) of the material. Is adenine really one of the few organic liquid crystals with NTE?

Story of adenine will be presented through two aspects: elegance of the laboratory temperature-resolved setup and complexity of simple-molecule adenine phase transformations.
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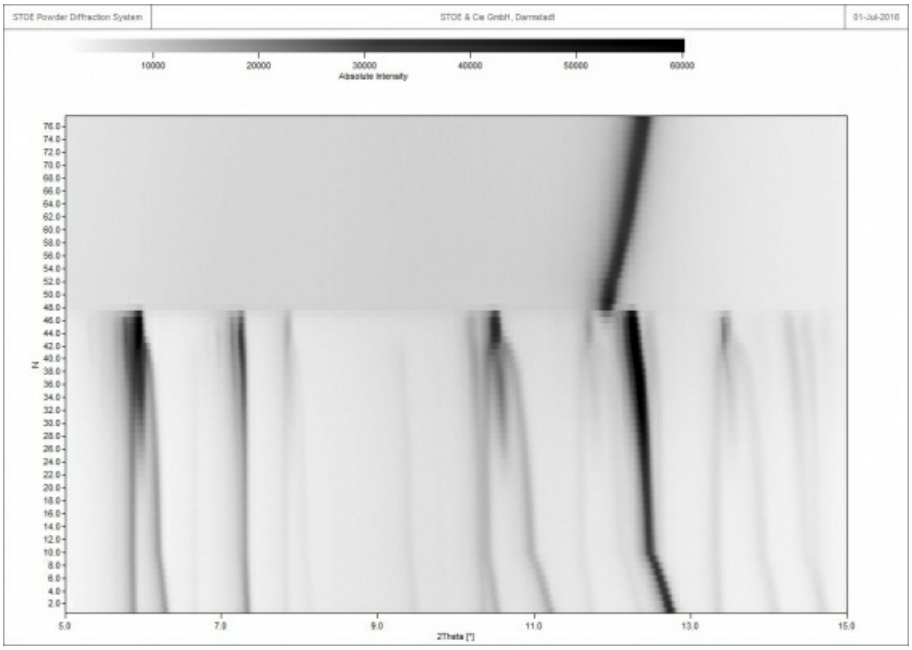

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