Crystal structure and tautomerism of Pigment Yellow 138 determined by X-ray powder diffraction and solid-state NMR

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Pigment Yellow 138 (P.Y. 138) is a commercial greenish-yellow pigment based on quinophthalone. It exhibits three possible tautomeric forms, which denoted as CH-form (1a), OH-form (1b) and NH-form (1c), Figure 1.

Due to the lack of good crystals for the single crystal X-ray diffraction analysis, the crystal structure of P.Y. 138 was determined by combining X-ray powder diffraction data (using real-space methods with subsequent Rietveld refinements) solid-state NMR and computational data. The tautomeric state was investigated by solid-state 1D and 2D multinuclear NMR experiments.

In the crystals, the compound exhibits the NH-tautomer with a hydrogen atom situated at the nitrogen of the quinoline moiety. Direct evidence of the presence of the NH-tautomer is provided by $^1$H-$^{15}$N HMQC solid-state NMR at very fast MAS (70 kHz). Solid-state dispersion-corrected density functional theory calculations with BLYP-D3 confirm the correctness of the crystal structure and support the NH-tautomer. The NH hydrogen atom forms an intramolecular resonance-assisted N-H•••O hydrogen bond to the neighbouring indandione moiety.

Figure 1. Possible tautomeric forms of P.Y. 138.