Structure of Pigment Yellow for Car Industry

Pigment Yellow 213 existing in two polymorphs is a new water-based coating compound

pigment yellow

Some years ago, automotive industry turned their interest from solvent-based to water-based coatings. This led to the requirement of novel water-dispersible pigments. Greenish-yellow shades appeared to be one of the most problematic, because all existing greenish-yellow pigments were either not dispersible in water or had an insufficient weather fastness, i.e. they faded out after a few years. Moreover, clear greenish-yellow shades cannot be achieved by mixing green and yellow pigments, since this would lead to dull shades. Due to these demands at the beginning of the last decade the Pigment Yellow 213 was developed (P.Y. 213, $C_{23}H_{21}N_5O_9$) as a new compound for water-based coatings. P.Y. 213 exists in at least in two polymorphs: the brown β-phase is formed as an intermediate product during synthesis. Subsequent heating in organic solvents to 423– 473 °K results in the greenish-yellow (lemon-yellow) α-phase. The phase shows good weather fastness and it does not agglomerate in water. Currently the α-phase is industrially used for water-based car coatings.

The challenge:	no single crystal due to low solubility; beam sensitivity; very low X-Ray pattern quality
Solution:	Automated 3D Diffraction Tomography in combination to X-Ray diffraction

Crystal structures of P.Y. 213 are not known. All attempts to grow single crystals failed, due to non-solubility in water or organic solvents, even at high temperatures. Furthermore, crystal growth from the melt or by sublimation is not possible either, because the pigment melts at 642 K with decomposition and does not sublime. The crystallinity of P.Y. 213 is never good, and thus X-ray powder data alone cannot be used directly for structure analysis.

Electron diffraction data were collected by automated 3D diffraction tomography .

The lattice parameters were accessed through a tilt (tilting interval of ±30, step size of 1°) of the crystal around an arbitrary axis, whereby diffraction patterns were collected automatically using an automated diffraction tomography (ADT) module. The crystal structure of the α-phase was finally solved combining XRPD and ADT data by real-space methods using recent developments of the program TOPAS. The α-polymorph of P.Y. 213 crystallizes in P-1, Z = 2. The molecule is almost planar. There are two intermolecular hydrogen bonds, both involving the NH groups of the two cis-amide fragments of the quinoxalinedione fragment. One of the NH groups forms an intermolecular hydrogen bond with a C=O group of a neighboring molecule, resulting in an eight-membered ring across an inversion centre, as is frequently found for cis-amide systems, e.g. in benzimidazolones.

The structure of α-P.Y. 213 (yellow phase) has been solved by the combination of electron diffraction, crystal-structure prediction using lattice-energy minimization and X-ray powder data, proving the power of today's real space methods. The PDF analysis of the phase is in agreement with the crystal structure.

Crystal Structure

$C_{23}H_{21}N_5O_9$

Triclinic $P\bar{1}$
a= 6.90 Å
b= 11.83 Å
c= 14.06 Å
α= 81.81°
β= 81.03°
γ= 87.54°

Experimental data

tilt range: ±30° step: 1°

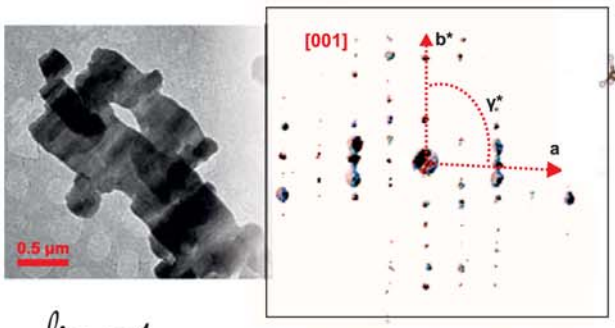

figure 1

TEM photograph of α-P.Y. 213 and 3D Reciprocal Space Reconstructed by 3D Diffraction Tomography Data

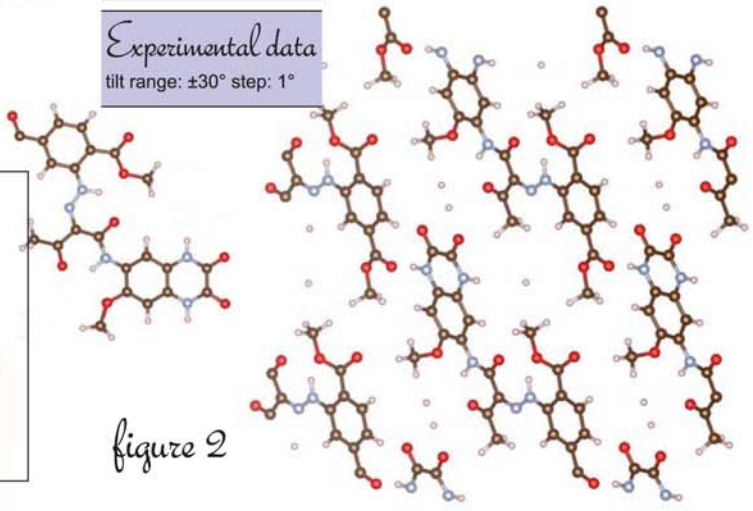

figure 2

Different Projections of Pigment Yellow 213 Crystal Structure

M. U. Schmidt et al *Acta Cryst. B* (2009) 65 189–199