# Supplementary Material

## for "The Crystal Structures of Six Industrial Benzimidazolone Pigments from Laboratory Powder Diffraction Data"

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### A.1. Crystal-Structure Determinations of β-P.O. 36, P.O. 62, P.Y. 151, α-P.Y. 154, β-P.Y. 181 and P.Y. 194

All six crystal structures were solved by real-space methods from laboratory X-ray powder diffraction data. The crystal structure solution of β-P.Y. 181 came chronologically first, has been published separately (Pidcock *et al.*, 2007) and was used as a template on which the crystal structure determinations of β-P.O. 36, P.O.62, P.Y. 151 and α-P.Y. 154 were based; these five crystal structures were solved with *DASH* (David *et al.*, 2006). For structure solution, the powder patterns were truncated to a real-space resolution of approximately 3 Å, which for CuKα$_1$ radiation corresponds to 30 °2θ. The backgrounds were subtracted with a high-pass filter (Brückner, 2000). The crystal structure of P.Y. 194 was solved with *MRIA* (Zlokazov & Chernyshev, 1992) and is described separately (see below).

### A.2. Indexing

For the six compounds mentioned in 3.1, accurate peak positions for indexing were obtained by fitting approximately 20 manually selected peaks with an asymmetry-corrected full Voigt function as implemented in the program *DASH* (David *et al.*, 2006). All six patterns could be indexed with the program *DICVOL91* (Boultif & Louër, 1991). For P.O. 62, α-P.Y. 154, β-P.Y. 181 and P.Y. 194 indexing was straightforward and reproducible, for P.Y. 151 indexing required some persistence; for β-P.O. 36 indexing took several days. The figures of merit $M(N)$ (de Wolff, 1968) and $F(N)$ (Smith & Snyder, 1979) are listed in Table A.I. All unit cells were transformed to their standard settings. The final unit-cell parameters, after Rietveld refinement, are given in Table III. Expected molecular volumes were calculated from single crystal data of known hydrazone pigments. The numbers of molecules in the unit cell were easily deduced from volume considerations (Tables A.I/III).

### A.3. Space-group Determination

β-P.O. 36, P.O. 62 and P.Y. 151 are triclinic, leaving space groups $P1$ or $P\text{-}1$; based on volume considerations, there are two molecules in the unit cell, which makes $P\text{-}1$ by far the more likely choice. The space groups of α-P.Y. 154 and β-P.Y. 181 were determined by means of Bayesian statistical analysis of the integrated intensities and their correlations (Markvardsen *et al.*, 2001); both were $P2_1/c$. For P.Y. 194, analysis of extinctions showed the following conditions limiting possible reflections: for $(h0l)$ reflections there are only reflections with $h + l = 2n$ and for $(0k0)$ reflections there are only reflections with $k = 2n$ in the pattern. It means that we have space group $P2_1/n$, which was transformed to its standard setting, $P2_1/c$. Because none of the six molecules contains an inversion centre, all asymmetric units must consist of a single molecule.

Table A.I. Indexing figures of Merit $M(N)$ and $F(N)$, Z, space groups and Pawley $\chi^2$ (from *DASH*) of the six pigments that were solved from powder data.

| | β-P.O. 36 | P.O. 62 | P.Y. 151 | α-P.Y. 154 | β-P.Y. 181 | P.Y. 194 |
|---|---|---|---|---|---|---|
| $N^1$ | 23 | 22 | 21 | 20 | 20 | 19 |
| $M(N)$ | 7.9 | 15.0 | 20.2 | 19.2 | 10.4 | 12.5 |
| $F(N)$ | 17.7 | 30.5 | 44.6 | 37.3 | 21.9 | 21.5 |
| Z | 2 | 2 | 2 | 4 | 4 | 4 |
| SpGr | $P$-1 | $P$-1 | $P$-1 | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| Pawley $\chi^2$ | 2.1 | 2.7 | 4.4 | 2.0 | 2.8 | 2.8 |

[1] $N$ = number of peaks selected for indexing.

## A.4. Crystal Structure Solution of β-P.O. 36, P.O. 62, P.Y. 151, α-P.Y. 154 and β-P.Y. 181

The crystal structures of β-P.O. 36, P.O. 62, P.Y. 151, α-P.Y. 154 and β-P.Y. 181 were solved by real-space methods using the program *DASH* (David *et al*., 2006). The background was subtracted with a high-pass filter (Brückner, 2000). Pawley refinement was used to extract integrated intensities and their correlations. The crystal structures were then solved from the powder patterns in direct space with simulated annealing. The P.O. 36, P.O. 62, P.Y. 151 and P.Y. 154 molecules all have seven possible flexible torsion angles, P.Y. 181 has ten. Combined with three translational and three orientational degrees of freedom, this corresponds to 13 or 16 degrees of freedom. However, because hydrazone pigments form intramolecular hydrogen bonds and because of the conjugated nature of the double and aromatic bonds, in most cases the statistical distribution of torsion angles in similar compounds is quite sharp, as can be seen from the Cambridge Structural Database (CSD, Allen (2002)), see *e.g.* Figure A1. *DASH* allows these sharp distributions to be exploited by restricting torsion angles to intervals of non-negligible probability, thereby significantly reducing the search space.
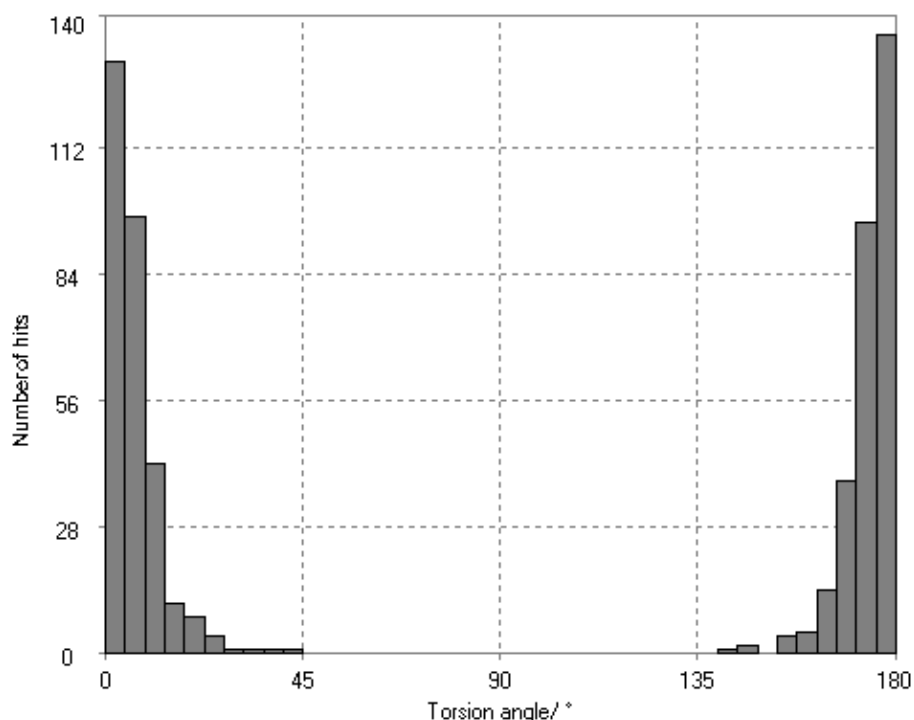


Figure A1. A torsion angle distribution from the CSD for the possible flexible torsion angle C⋯C−N−N= in a hydrazone molecule. The distribution shows that the torsion angle is planar within +/- 15°, at either 0° or 180°. This information can be used in *DASH* to speed up the crystal structure solution.

Suppl. Mat for Acta Cryst (2009) B65, 200-211

2

The starting molecular geometries for P.Y. 151, P.Y. 154 and P.Y. 181 were obtained by *in vacuo* energy-minimisation with Gaussian03 (Frisch *et al.*, 2003) at the SCF-HF/6-31G\*\* level; for P.O. 36 and P.O. 62 a geometry from a force-field minimisation was used.

As there are only a maximum of 16 degrees of freedom, the default settings of *DASH* were used for the parameters that control the simulated annealing, except for the number of simulated annealing runs, which was increased from 10 to 50 to get better statistics regarding reproducibility.

In 50 simulated annealing runs, the correct crystal structure was found 47, 47, 50, 50 and 11 times for β-P.O. 36, P.O. 62, P.Y. 151, α-P.Y. 154 and β-P.Y. 181 respectively. The crystal structures were judged to be correct based on the presence of extensive intra- and intermolecular hydrogen bonding, the absence of short non-bonded contacts and the visual fit to the experimental pattern.

### A.5. Crystal Structure Solution of P.Y. 194

The crystal structure of P.Y. 194 was solved by real-space methods using the program *MRIA* (Zlokazov & Chernyshev, 1992). For the indexing solution that gave acceptable unit-cell parameters and unit-cell volume a full pattern decomposition procedure was done with the Pawley method. In *MRIA* the pattern was fitted using split-type pseudo-Voigt peak profile functions (Toraya, 1986). The background was manually divided into three parts and each part was fitted with a Chebyshev polynomial.

The starting model of the molecule was built in Cartesian coordinates from the data of the P.Y. 154 molecule; the molecular geometry was kept fixed during crystal structure solution.

The position and the orientation of the molecule in the unit cell were found with *MRIA* using a grid search technique (Chernyshev & Schenk, 1998).

### A.6. Crystal Structure Solution of θ-P.Y. 181

The crystal structure of the θ polymorph of P.Y. 181 was solved from powder data. The θ phase turned out to be the dimethylsulfoxide *N*-methyl-2-pyrrolidone solvate. The details of the structure solution are described elsewhere (van de Streek, 2008).

### A.7. Attempts to Solve the Crystal Structure of β-P.O. 72

Considerable effort was made to determine the crystal structure of the β phase of P.O. 72 by global lattice energy minimisations using the program *CRYSCA* (Schmidt & Kalkhof, 1997). In *CRYSCA* the lattice energy is calculated as the sum of Van der Waals interactions and Coulomb energy. Starting from a set of many thousands of randomly generated crystal structures the energies are optimised until a minimum is reached. The minima are sorted according to energy and checked for reasonable molecular geometries and intermolecular interactions. Different molecular conformations and various space groups were tested. All low-energy minima showed reasonable geometries and extensive hydrogen bonding. For all low-energy structures, X-ray powder diagrams were simulated and compared to the experimental powder diagram. But no good match could be found. Global lattice energy minimisations using the "Polymorph Predictor" within the Cerius[2] package gave no better result either. The best fit between calculated and experimental powder diagrams was achieved by taking a low energy structure from *CRYSCA* and manually shifting the molecular layers against each other. The simulated X-ray powder diagram (Figure A2) still deviates considerably from the experimental one (Figure 4), but a better fit could not be achieved with a reasonable molecular model and reasonable intermolecular interactions.
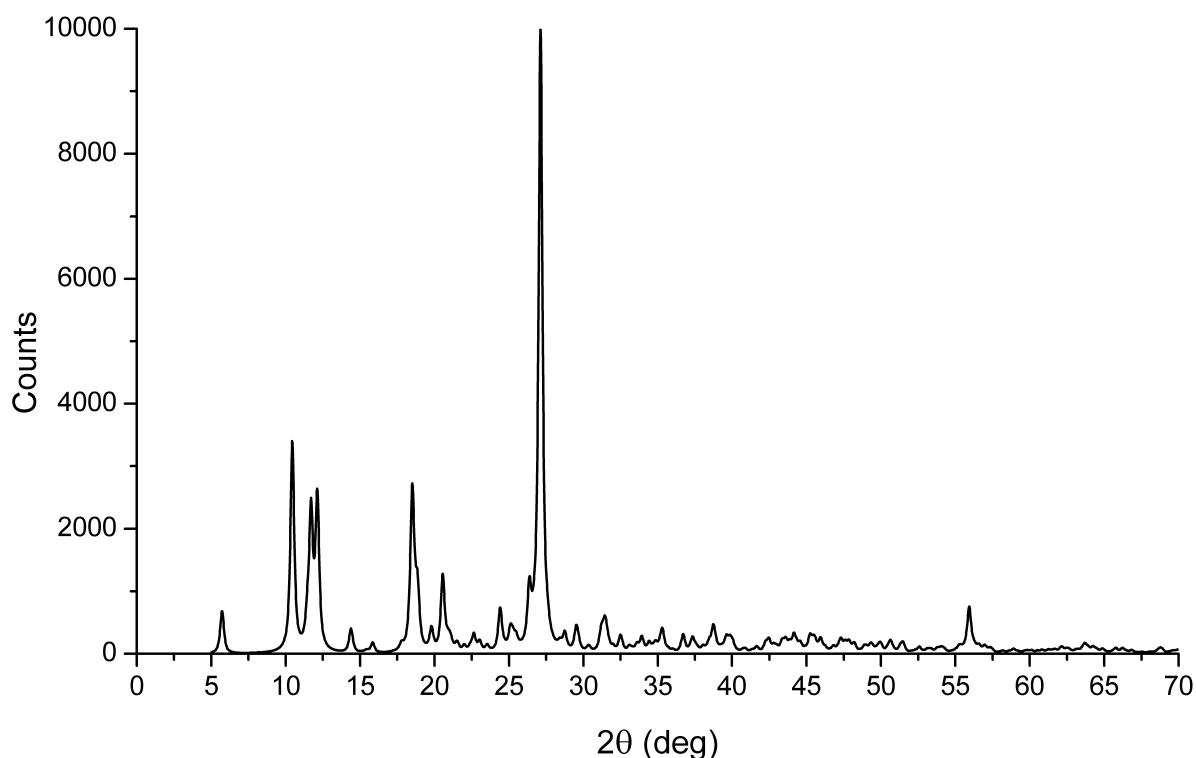
Figure A2. Calculated powder diffraction pattern of β-P.O. 72.

In the proposed structure, the hydrogen-bond pattern would be the same as for BIRZIL. This is experimentally supported by infrared spectroscopy: The IR spectra of β-P.O. 72 and BIRZIL are quite similar, also in the region 1400 to 1800 cm$^{-1}$, which is sensitive to the hydrogen bond pattern. In contrast, the IR spectrum of γ-P.O. 72 is less similar to those of β-P.O. 72 or BIRZIL.

According to the proposed model, β-P.O. 72 should be isostructural to P.Y. 13 and P.Y. 14 (Schmidt, 1999, Schmidt *et al.*, 2007). This is supported by similarities between the X-ray powder diagrams of β-P.O. 72, P.Y. 13 and P.Y. 14. The molecular structures of P.Y. 13 and P.Y. 14 differ from P.O. 72 only by a replacement of the benzimidazolone moieties of P.O. 72 by 2,4-dimethylphenyl or 2-methylphenyl groups respectively.

Nevertheless the correct crystal structure of β-P.O. 72 remains obscure and the structure given here should be regarded only as a first approximation to the actual structure.

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