

Crystal structure of Pigment Red 254 from X-ray powder diffraction data

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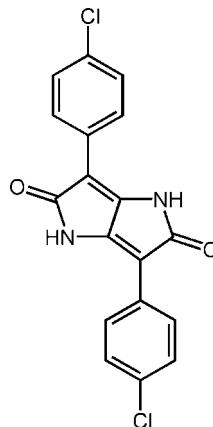
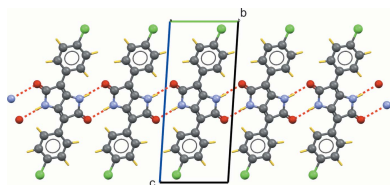
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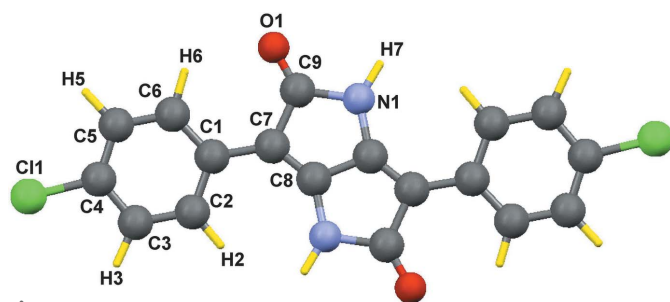
The crystal structure of Pigment Red 254 [P.R. 254, C₁₈H₁₀Cl₂N₂O₂; systematic name: 3,6-bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione] was solved from laboratory X-ray powder diffraction data using the simulated annealing method followed by Rietveld refinement because the very low solubility of the pigment in all solvents impedes the growth of single crystals suitable for X-ray analysis. The molecule lies across an inversion center. The dihedral angle between the benzene ring and the pyrrole ring in the unique part of the molecule is 11.1 (2)°. In the crystal, molecules are linked *via* N—H···O hydrogen bonds, forming chains along [110] incorporating R₂²(8) rings.

1. Chemical context

Within the range of diketopyrrolo-pyrrole (DPP) pigments presently offered to the market, P.R. 254 plays the most important role (Herbst & Hunger, 2004), this commercially available type the pigment being widely used in industrial paints, for example for automotive finishes, and plastics which are processed at high temperature. P.R. 254 affords medium shades of red in full shades, while reductions made with a white paint are somewhat bluish red. The pigment demonstrates excellent fastness to organic solvents and weather-fastness, as well as good coloristic and fastness properties. It also shows good hiding power and high tinctorial strength.

The pigment exhibits very low solubility in all solvents, impeding the growth of single crystals suitable for X-ray analyses. Pigments are not dissolved in their application media, but finely dispersed. Consequently the final product properties depend on the crystal structure of the pigments. The crystal structure was successfully solved from laboratory X-ray powder diffraction data using the simulated annealing method followed by Rietveld refinement.




Figure 1

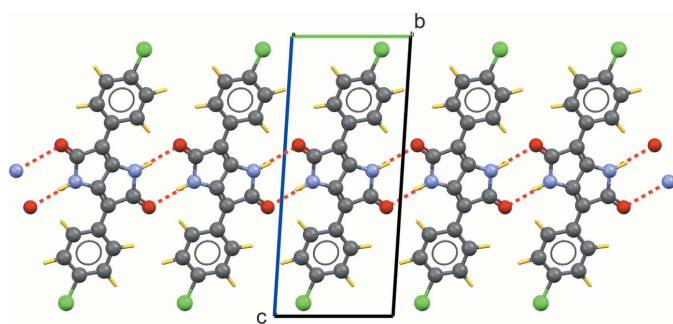
The molecular structure of the title compound. Unlabelled atoms are related by the symmetry code $(-x + 1, -y + 1, -z + 1)$. The atoms are represented by spheres of arbitrary size.

2. Structural commentary

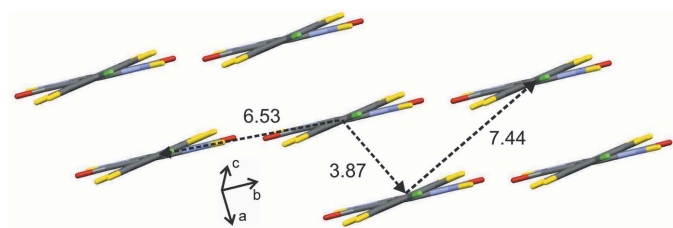
The molecule of the title compound (Fig. 1) lies across an inversion center. The dihedral angle between the benzene (C1–C6) and pyrrole (N1/C7–C9/C8) rings is $11.1(2)^\circ$. In the crystal, molecules are linked *via* N–H \cdots O hydrogen bonds, forming one-dimensional chains along [110] incorporating $R_2^2(8)$ rings. One part of the molecule (C1/C2/C3/C4/C5/C6) and the pyrrole ring [C7/C9/N1/C8/C8($-x + 1, -y + 1, -z + 1$)] is $11.1(2)^\circ$. An intramolecular C–H \cdots O hydrogen bond occurs (Table 1).

3. Supramolecular features

In the crystal, molecules are linked *via* N–H \cdots O hydrogen bonds, forming chains along [110] incorporating $R_2^2(8)$ rings


Figure 2

Part of the crystal structure of the title compound (viewed along the *a* axis). Hydrogen bonds are shown as dashed lines.


Figure 3

Layered arrangement in the crystal structure of the title compound. Numerical values refer to distances in Å.

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
N1–H7 \cdots O1 ⁱ	0.985 (17)	1.904 (18)	2.884 (5)	173 (2)
C2–H2 \cdots O1 ⁱⁱ	1.04 (2)	2.542 (18)	3.489 (6)	151.2 (16)
C2–H2 \cdots N1 ⁱⁱⁱ	1.04 (2)	2.55 (2)	3.255 (6)	124.8 (11)
C6–H6 \cdots O1	1.062 (14)	2.28 (2)	2.959 (6)	119.9 (14)

Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $x - 1, y - 1, z$; (iii) $-x + 1, -y + 1, -z + 1$.

(Fig. 2). In addition, π – π stacking interactions between symmetry-related benzene rings with a centroid–centroid distance of $3.871(2)^\circ$ connect these chains along [100] (Fig. 3).

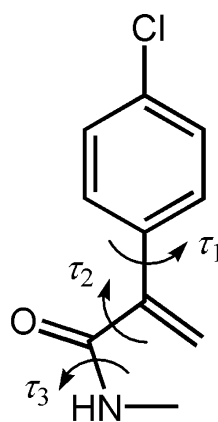
4. Synthesis and crystallization

The technical product P.R. 254 (TR008.052.11-F) supplied by Clariant Produkte (Deutschland) GmbH was taken as is.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Rietveld refinement was carried out with *TOPAS* (Coelho, 2007) using all diffraction data. The *TOPAS* input file (including all crystallographic constraints and chemical restraints) was generated automatically by the *DASH-to-TOPAS* link.

Simulated annealing method (SA) was used to solve the crystal structure from the powder pattern in direct space. The starting molecular geometry was built from known crystal structure of similar compound from the Cambridge Structural Database (CSD; Groom *et al.*, 2016). The half of the molecule has three flexible torsion angles, which combined with three



τ_1	free	-180° to 0° and 0° to 180°
τ_2	unimodal	-10° to -2°
τ_3	unimodal	170° to 190°

Figure 4

The three flexible torsion angles and their allowed ranges in the structure solution step.

Table 2

Experimental details.

Crystal data	
Chemical formula	C ₁₈ H ₁₀ Cl ₂ N ₂ O ₂
<i>M_r</i>	357.19
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	3.871 (1), 6.553 (1), 15.292 (1)
α , β , γ (°)	92.773 (3), 94.656 (3), 99.627 (2)
<i>V</i> (Å ³)	380.45 (3)
<i>Z</i>	1
Radiation type	Cu K α ₁ , λ = 1.54056 Å
Specimen shape, size (mm)	Flat sheet, 10 × 10 × 1
Data collection	
Diffractometer	Stoe Stadi-P with linear PSD
Specimen mounting	Sample was prepared between two polyacetate films
Data collection mode	
Scan method	Transmission
2 θ values (°)	Step 2 θ_{\min} = 2.00 2 θ_{\max} = 60.00 2 θ_{step} = 0.01
Refinement	
<i>R</i> factors and goodness of fit	<i>R_p</i> = 6.506, <i>R_{wp}</i> = 8.578, <i>R_{exp}</i> = 7.467, χ^2 = 1.320
No. of parameters	115
No. of restraints	44
H-atom treatment	All H-atom parameters refined

Computer programs: WINX^{POW} (Stoe & Cie, 2004), TOPAS-Academic (Coelho, 2007), DASH3.1 (David *et al.*, 2006) and Mercury (Macrae *et al.*, 2008).

translational and three orientational degrees of freedom corresponds to a total of nine degrees of freedom. The program DASH (David *et al.*, 2006) was used for structure solution. DASH allows the torsion angles to be restricted to intervals that significantly reduce the search space. These three flexible torsion angles and their allowed ranges are shown in Fig. 4. The powder pattern was truncated to a real space resolution of 2.6 Å, which for Cu K α ₁ radiation corresponds to 34.6° in 2 θ . The background was subtracted with a Bayesian high-pass filter (David & Sivia, 2001). The number of SA runs was increased to 50 to get better statistics regarding reproducibility. The background subtraction, peak fitting, Pawley refinement and SA algorithms were used as implemented in the program DASH.

Accurate peak positions for indexing were obtained by fitting 20 manually selected peaks with an asymmetry-corrected Voigt function. Indexing was done with the program DICVOL91 (Boultif & Louër, 1991). A triclinic unit cell was determined with $M(20) = 40.7$ (de Wolff *et al.*, 1968), $F(20) = 82.8$ (Smith & Snyder, 1979). From volume considerations, the unit cell can contain one molecule of P.R. 254 (*Z* = 1). The molecule has an inversion centre, which means the asymmetric unit must consist of a one half of the molecule.

Pawley refinement (Pawley, 1981) was carried out for refining the background, unit-cell parameters, zero-point error, peak-width and peak-asymmetry parameters. It allows extracting integrated intensities and their correlations. All intensities were refined without reference to a structural model and the result is the best fit that is theoretically possible: $R_{wp} = 13.57$, $R_{exp} = 11.20$, $\chi^2 = 1.467$.

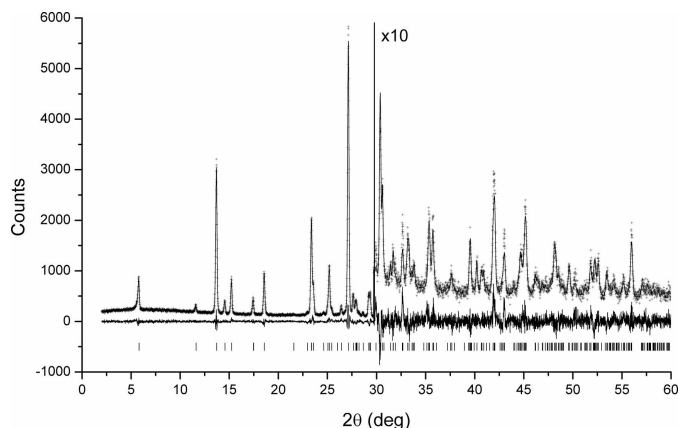


Figure 5

Rietveld plot of P.R. 254. The experimental data points are shown as crosses, the calculated pattern as a solid line and the difference curve as a line under the profiles. Tick marks are shown as vertical dashes (laboratory data).

Suitable chemical restraints were applied for all bond lengths, valence angles and the planarity of the aromatic ring systems (including the five-membered condensed system). Anisotropic peak broadening was included to allow the peak profiles to be described accurately. The discrepancies between the observed and the calculated profile appeared to systematically depend on the *hkl* indices of the reflections, indicating preferred orientation in the [001] direction. The March–Dollase formula (Dollase, 1986) was used. The diffraction profiles and the differences between the measured and calculated profiles are shown in Fig. 5.

Acknowledgements

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Computing details

Data collection: *WINXP^{OW}* (Stoe & Cie, 2004); cell refinement: *TOPAS-Academic* (Coelho, 2007); data reduction: *DASH3.1* (David *et al.*, 2006); program(s) used to solve structure: *DASH3.1* (David *et al.*, 2006); program(s) used to refine structure: *TOPAS-Academic* (Coelho, 2007); molecular graphics: *Mercury* (Macrae *et al.*, 2008).

3,6-Bis(4-chlorophenyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione

Crystal data

$C_{18}H_{10}Cl_2N_2O_2$	$V = 380.45 (3) \text{ \AA}^3$
$M_r = 357.19$	$Z = 1$
Triclinic, $P\bar{1}$	$D_x = 1.57 \text{ Mg m}^{-3}$
$a = 3.871 (1) \text{ \AA}$	Cu $K\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$
$b = 6.553 (1) \text{ \AA}$	$T = 293 \text{ K}$
$c = 15.292 (1) \text{ \AA}$	Particle morphology: powder
$\alpha = 92.773 (3)^\circ$	red
$\beta = 94.656 (3)^\circ$	flat_sheet, $10 \times 10 \text{ mm}$
$\gamma = 99.627 (2)^\circ$	

Data collection

Stoe Stadi-P with linear PSD diffractometer	Specimen mounting: sample was prepared between two polyacetate films
Radiation source: sealed X-ray tube	Data collection mode: transmission
Primary focussing, Ge 111 monochromator	Scan method: step
	$2\theta_{\min} = 2.00^\circ$, $2\theta_{\max} = 60.00^\circ$, $2\theta_{\text{step}} = 0.01^\circ$

Refinement

Refinement on I_{net}	44 restraints
Least-squares matrix: full with fixed elements per cycle	0 constraints
$R_p = 6.506$	All H-atom parameters refined
$R_{\text{wp}} = 8.578$	Weighting scheme based on measured s.u.'s $w = 1/\sigma[Y_{\text{obs}}]^2$
$R_{\text{exp}} = 7.467$	$(\Delta/\sigma)_{\max} = 0.001$
5800 data points	Background function: Chebyshev function with 20 terms
Excluded region(s): none	Preferred orientation correction: March–Dollase formula (Dollase, 1986), (001) direction
Profile function: fundamental parameters	
115 parameters	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8418 (7)	0.4738 (6)	0.6911 (3)	0.05373
C2	0.7516 (10)	0.2631 (7)	0.7088 (3)	0.05373

C3	0.8543 (9)	0.1967 (6)	0.7905 (3)	0.05373
C4	1.0452 (8)	0.3351 (7)	0.8528 (3)	0.05373
C5	1.1403 (8)	0.5402 (7)	0.8377 (3)	0.05373
C6	1.0380 (9)	0.6065 (7)	0.7573 (3)	0.05373
C7	0.7380 (7)	0.5404 (6)	0.6038 (3)	0.05373
C8	0.4818 (10)	0.5527 (8)	0.4587 (4)	0.05373
C9	0.8702 (6)	0.7478 (4)	0.5715 (2)	0.05373
H2	0.606 (5)	0.157 (2)	0.6614 (15)	0.06447
H3	0.796 (4)	0.039 (2)	0.8095 (13)	0.06447
H5	1.286 (4)	0.644 (2)	0.8892 (16)	0.06447
H6	1.113 (4)	0.767 (2)	0.7484 (14)	0.06447
H7	0.774 (5)	0.879 (2)	0.4529 (17)	0.06447
O1	1.0679 (7)	0.8859 (6)	0.6108 (3)	0.05373
N1	0.7025 (7)	0.7478 (5)	0.4806 (3)	0.05373
Cl1	1.1601 (7)	0.2385 (4)	0.9528 (3)	0.05373

Geometric parameters (Å, °)

C1—C2	1.411 (6)	C3—H3	1.08 (2)
C1—C6	1.388 (5)	C5—H5	1.07 (2)
C1—C7	1.470 (6)	C6—H6	1.06 (1)
C2—C3	1.392 (6)	C9—O1	1.186 (4)
C3—C4	1.362 (6)	C9—N1	1.485 (5)
C4—C5	1.369 (6)	N1—C8	1.422 (5)
C5—C6	1.374 (6)	N1—H7	0.98 (2)
C7—C9	1.492 (5)	C4—Cl1	1.736 (6)
C2—H2	1.04 (2)		
C2—C1—C6	117.3 (4)	C2—C3—H3	125 (1)
C2—C1—C7	119.3 (3)	C4—C3—H3	115 (1)
C6—C1—C7	123.4 (3)	C6—C5—H5	122 (1)
C1—C2—C3	120.0 (3)	C4—C5—H5	119 (1)
C1—C6—C5	122.5 (4)	C7—C9—O1	126.8 (4)
C1—C7—C9	124.4 (3)	C7—C9—N1	106.4 (2)
C2—C3—C4	119.8 (4)	C9—N1—C8	108.8 (4)
C6—C5—C4	118.5 (4)	O1—C9—N1	126.8 (3)
C3—C4—C5	121.8 (4)	C3—C4—Cl1	116.6 (4)
C1—C2—H2	120 (1)	C5—C4—Cl1	121.6 (3)
C3—C2—H2	119.7 (9)	C9—N1—H7	113 (1)
C1—C6—H6	121 (1)	C8—N1—H7	138 (1)
C5—C6—H6	116 (1)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H7 \cdots O1 ⁱ	0.985 (17)	1.904 (18)	2.884 (5)	173 (2)
C2—H2 \cdots O1 ⁱⁱ	1.04 (2)	2.542 (18)	3.489 (6)	151.2 (16)

C2—H2···N1 ⁱⁱⁱ	1.04 (2)	2.55 (2)	3.255 (6)	124.8 (11)
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Symmetry codes: (i) $-x+2, -y+2, -z+1$; (ii) $x-1, y-1, z$; (iii) $-x+1, -y+1, -z+1$.