Crystal Structure of Pigment Yellow 138 Derivative

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An X-ray analysis of the title pigment was undertaken to understand the structure–stability relationships. The molecule takes a non-planar structure, because of the 2-(inden-2-yl)quinoline and isoindoline fragments being twisted at the C8–N21 bond. The dihedral angles between three planar moieties are 4.2(3) and 64.4(3)°. In the crystal structure, the flat 2-(inden-2-yl)quinoline fragments are stacked opposed to each other. The isoindoline rings sandwich the solvent molecules. The solvent molecule sits on a crystallographic center of symmetry, and is disordered in the solvent channels along the c-axis.

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The title compound, 2-(1,2-dihydro-2-(1,3-dioxo-1*H*-inden-2(3*H*)-ylidene)quinolin-8-yl)isoindoline-1,3-dione, (**I**), is a type of quinophthalone yellow. A series of the pigments are manufactured on a large scale, and are of significant commercial importance worldwide, as well as C.I. Pigment Yellow 138 (PY-138); CAS No. 30125-47-4, (**II**). To understand the structure–stability relationships, we conducted an X-ray analysis of the title compound.

The dechlorinated compound (**I**), which consists of the skeleton of PY-138, was prepared by a modifying method

reported by Malanker *et al.*¹ from 8-amino-2-methylquinoline and phthalic anhydride, purchased from Tokyo Chemical Industry (Tokyo). Crystals were obtained from a toluene solution with slow evaporation at room temperature. A plate-like yellow crystal of 0.4 × 0.4 × 0.2 mm in size was used for diffraction experiments.

The crystal and experimental data are given in Table 1. The structure was solved by direct methods using the program SIR88,² and refined by full-matrix least-squares. Non-hydrogen atoms, except for the solvent molecule, were refined anisotropically. The solvent molecule was disordered, and the coordinates of all atoms were rigidly refined and finally fixed. All hydrogen atoms of the pigment molecule were determined from difference Fourier maps and refined isotropically. The atomic parameters for the non-hydrogen atoms are listed in

Fig. 1 Chemical structure.

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Table 1 Crystal and experimental data

Formula: C₂₆H₁₄N₂O₄·0.5 (C₇H₈)

Formula weight: 464.48

Crystal system: triclinic

Space group: *P* $\bar{1}$

Z = 2

a = 12.436(4) Å

b = 12.564(4) Å

c = 7.781(5) Å

α = 107.48(4)°

β = 92.14(4)°

γ = 79.931(3)°

V = 1141.7(9) Å³

*D*_x = 1.35 g/cm³

No. of reflections used = 4702

2 θ _{max} = 149.9° with Cu K α

R = 0.077

(Δ / σ)_{max} = 0.0001

($\Delta\rho$)_{max} = 0.39 eÅ⁻³

($\Delta\rho$)_{min} = -0.32 eÅ⁻³

Measurement: Enraf-Nonius CAD4

Program system: teXsan

Structure determination: direct method (SIR88)

Refinement: full-matrix least-squares

Table 2 Atomic coordinates and equivalent isotropic thermal parameters (B_{eq})

Atom	x	y	z	$B_{eq}/\text{\AA}^2$
O11	-0.0634 (2)	-0.1454 (1)	0.5919 (3)	5.08 (4)
O13	-0.1358 (2)	0.2545 (2)	0.7884 (3)	6.10 (5)
O20	-0.3348 (2)	-0.2440 (2)	0.6209 (3)	6.07 (5)
O22	-0.2139 (2)	-0.3803 (2)	0.0374 (3)	5.89 (5)
N1	-0.2523 (2)	-0.0586 (2)	0.4734 (3)	4.30 (5)
N21	-0.2847 (2)	-0.2842 (2)	0.3235 (3)	4.25 (5)
C2	-0.2295 (2)	0.0453 (2)	0.5571 (4)	4.25 (5)
C3	-0.3067 (2)	0.1398 (2)	0.5341 (4)	4.87 (6)
C4	-0.3936 (2)	0.1212 (2)	0.4296 (4)	4.98 (6)
C5	-0.5003 (2)	-0.0139 (3)	0.2207 (4)	5.35 (7)
C6	-0.5116 (3)	-0.1229 (3)	0.1336 (5)	5.88 (8)
C7	-0.4396 (2)	-0.2129 (3)	0.1674 (4)	5.38 (7)
C8	-0.3558 (2)	-0.1925 (2)	0.2842 (4)	4.44 (6)
C9	-0.3391 (2)	-0.0817 (2)	0.3670 (3)	4.21 (5)
C10	-0.4137 (2)	0.0101 (2)	0.3377 (4)	4.52 (6)
C11	-0.0562 (2)	-0.0451 (2)	0.6645 (4)	4.38 (6)
C12	-0.1338 (2)	0.0536 (2)	0.6552 (4)	4.37 (6)
C13	-0.0936 (2)	0.1551 (2)	0.7591 (4)	4.67 (6)
C14	0.0847 (3)	0.1781 (3)	0.9415 (4)	5.54 (7)
C15	0.1779 (3)	0.1188 (3)	0.9981 (5)	6.09 (8)
C16	0.1978 (3)	0.0014 (3)	0.9438 (5)	6.06 (8)
C17	0.1282 (2)	-0.0612 (3)	0.8347 (4)	5.30 (7)
C18	0.0346 (2)	-0.0022 (2)	0.7783 (4)	4.59 (6)
C19	0.0141 (2)	0.1157 (2)	0.8336 (4)	4.79 (6)
C20	-0.2838 (2)	-0.3054 (2)	0.4893 (4)	4.55 (6)
C22	-0.2221 (2)	-0.3752 (2)	0.1926 (4)	4.46 (6)
C23	-0.1063 (3)	-0.5609 (2)	0.2228 (5)	5.73 (7)
C24	-0.0756 (3)	-0.6212 (3)	0.3425 (5)	6.29 (8)
C25	-0.1113 (3)	-0.5812 (3)	0.5187 (6)	6.42 (9)
C26	-0.1795 (3)	-0.4760 (3)	0.5849 (5)	5.63 (8)
C27	-0.2099 (2)	-0.4160 (2)	0.4642 (4)	4.54 (6)
C28	-0.1738 (2)	-0.4565 (2)	0.2882 (4)	4.59 (6)
C29	0.4509	-0.4523	-0.1418	18.9 (4)
C30	0.3964	-0.4395	0.0263	16.2 (3)
C31	0.4464	-0.4871	0.1671	19.7 (4)
C32	0.3776	-0.3895	-0.2645	30.0

$$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}(a_i\cdot a_j).$$

Fig. 2 ORTEP-3 drawing representing heavy atoms as 50% probability ellipsoids and H atoms as circles of arbitrary size. The dashed bonds show intramolecular hydrogen bonds.

Table 2. All calculations were carried out with the program package teXsan.³

An ORTEP-3⁴ drawing of the compound (**I**) together with the atomic numbering is shown in Fig. 2. The ring-labeling system is shown in Fig. 1. Selected bond distances, bond angles and torsion angles are given in Table 3. The molecule takes a non-planar structure, because of two planar fragments (2-(inden-2-yl)quinoline A - D and isoindoline EF) being twisted at the

Table 3 Selected bond distances ($\text{\AA}$), bond angles ($^\circ$) and torsion angles ($^\circ$)

Bond	distances ($\text{\AA}$)	Bond	distances ($\text{\AA}$)
O11-C11	1.234(3)	O13-C13	1.223(3)
O20-C20	1.204(3)	O22-C22	1.198(3)
N1-C2	1.347(3)	N1-C9	1.355(4)
N21-C8	1.428(3)	N21-C20	1.392(4)
N21-C22	1.414(3)	C2-C3	1.442(4)
C2-C12	1.392(4)	C3-C4	1.339(4)
C4-C10	1.426(4)	C5-C6	1.363(5)
C5-C10	1.398(4)	C6-C7	1.400(4)
C7-C8	1.364(4)	C8-C9	1.396(4)
C9-C10	1.418(3)	C11-C12	1.450(4)
C12-C13	1.450(4)		
Bond angles ($^\circ$)		Bond angles ($^\circ$)	
C2-N1-C9	125.9(2)	C8-N21-C20	123.4(2)
C8-N21-C22	124.3(2)	C20-N21-C22	111.3(2)
N1-C2-C3	116.4(3)	N1-C2-C12	118.4(2)
C3-C2-C12	125.2(3)	N21-C8-C7	120.3(2)
N21-C8-C9	119.4(2)	C7-C8-C9	120.3(3)
C2-C12-C11	122.5(2)	C2-C12-C13	128.3(2)
C11-C12-C13	109.2(2)		
Torsion angles ($^\circ$)		Torsion angles ($^\circ$)	
N1-C2-C12-C11	2.5(4)	C3-C2-C12-C13	2.8(5)
C9-N1-C2-C12	-177.1(3)	C4-C3-C2-C12	176.9(3)
C7-C8-N21-C22	58.1(4)	C9-C8-N21-C20	70.0(3)
N21-C8-C7-C6	177.8(3)	N21-C8-C9-C10	-175.9(2)

C8-N21 bond. The dihedral angles between three planar moieties consisting of two fused-rings are as follows: AB/CD $4.2(3)$ and AB/EF $64.4(3)^\circ$. The AB and CD moieties make a flat plane with a mean deviation of $0.053(3)\text{\AA}$. The O11, O13, O20 and O22 atoms lie in the least-square planes calculated from two fused-rings, with mean deviations of $0.011(4)$, $0.038(5)$, $0.065(5)$ and $0.064(5)\text{\AA}$, respectively. Electron localization was found at the C2-C12 bond with a distance of $1.392(4)\text{\AA}$. The planarity of fragment A - D is also stabilized by two asymmetrical intramolecular hydrogen bonds ($\text{N1-H}\cdots\text{O11} = 2.665(4)\text{\AA}$ and $\text{C3-H}\cdots\text{O13} = 3.090(4)\text{\AA}$). The fragment A - D bonds in-plane at the C2-C12 bond in the direction of the N1 atom, with the summed bond-angles of N1-C2-C12-C11 and C3-C2-C12-C13 being $240.9(3)$ and $253.5(4)^\circ$.

In the crystal structure, there is no significant intermolecular hydrogen bond. The flat A - D fragments are stacked opposed to each other. The solvent molecules insert into the stacked EF fragments perpendicular to the A - D fragments. The solvent molecule sits on a crystallographic center of symmetry, and is disordered in the solvent channels along the *c*-axis.

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