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3,6-Di-4-pyridylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

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3,6-Di-4-pyridylpyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione

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Key indicators

Single-crystal X-ray study
 $T = 93\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$
 R factor = 0.241
 wR factor = 0.565
 Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The centrosymmetric title compound, $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$, is an organic red pigment utilized for H_2 gas sensors. The centrosymmetric diketopyrrolopyrrole moieties are connected by bifurcated $\text{N}\cdots\text{H}\cdots\text{O}$ hydrogen bonds to form a ribbon structure along $[110]$ and $[1\bar{1}0]$ alternately. The molecules are stacked in a 'hunter's fence' (*viz.* when viewed from the side, molecules, slipped by 45° within molecular stacks, cross each other in a fence-like structure) fashion along the a axis.

Comment

Diketodiphenylpyrrolopyrroles are industrially important red pigments (Herbst & Hunger, 1993). The title compound, (I) (*p*-DPPP), is a dipyridyl derivative that possesses a high proton affinity because of the N atom of the pyridyl ring. A drastic change in color as well as electrical conductivities have been observed due to protonation at the N atom (Mizuguchi, 1993). Because of this, *p*-DPPP has newly attracted attention as a material for H_2 gas sensors (Takahashi & Mizuguchi, 2005). Recently, we found that there exist two crystal phases: one is quite sensitive to protons (phase I, grown from the vapor phase) while the other exhibits a poor proton affinity (phase II, recrystallized from solution). The structure of phase II has been previously reported (Mizuguchi *et al.*, 2002). This phase is characterized by two $\text{N}-\text{H}\cdots\text{O}$ intermolecular hydrogen bonds (between the NH group of one molecule and the carbonyl O atom of the neighboring one) and two $\text{N}-\text{H}\cdots\text{N}$ bonds (between the NH group and the N atom of the pyridyl ring). That is, one of the N atoms of two pyridyl rings in *p*-DPPP is blocked by the formation of $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds. Therefore, the number of N atoms available for the protonation is reduced by half. The purpose of the present investigation is to determine the structure of phase I in order to account for its high proton affinity.

Fig. 1 shows the molecular structure of (I). The molecule is centrosymmetric but not entirely planar; the angle between each pyridyl ring and the central heterocyclic ring system is

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Figure 1

A view of the molecular structure of (I), showing 30% displacement ellipsoids for non-H atoms. The unlabeled atoms are related by the symmetry code $(1-x, 1-y, 1-z)$.

6.4 (3)° (Table 1). Fig. 2 shows the projection of the structure on to the bc plane. The p -DPPP molecules are connected by $N-H\cdots O$ bifurcated hydrogen bonds to form a ribbon structure along $[110]$ and $[1\bar{1}0]$ alternately (Table 2). It is apparent that there are no $N-H\cdots N$ hydrogen bonds and that two N atoms of the pyridyl rings remain free (*i.e.* unbonded) for accepting protons, quite in contrast to phase II. This explains why phase I is quite sensitive to protons. It is also to be noted that there is a small step of about 0.40 Å between hydrogen-bonded molecular planes as shown in Fig. 3. The molecules are stacked in a 'hunter's fence' fashion along the a axis.

Experimental

DPPP was synthesized according to the method reported previously by Rochat *et al.* (1986) and purified three times by sublimation using a two-zone furnace (Mizuguchi, 1981). Single crystals of DPPP were grown from the vapor phase in a closed system based on a two-zone furnace. After 48 h, a number of single crystals were obtained in the form of platelets. However, these were quite thin and mostly curved.

Crystal data

$C_{16}H_{10}N_4O_2$
 $M_r = 290.28$
 Monoclinic, $P2_1/n$
 $a = 3.722$ (1) Å
 $b = 6.263$ (3) Å
 $c = 26.506$ (9) Å
 $\beta = 94.41$ (2)°
 $V = 616.0$ (4) Å³
 $Z = 2$

$D_x = 1.565$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 4967 reflections
 $\theta = 3.3$ –68.3°
 $\mu = 0.89$ mm⁻¹
 $T = 93.2$ K
 Platelet, red
 $0.20 \times 0.10 \times 0.02$ mm

Figure 2

Projection on to the bc plane, showing $N-H\cdots O$ intermolecular hydrogen bonds as thin lines.

Figure 3

Side view of the hydrogen-bonded molecules, showing a step of about 0.4 Å.

Data collection

Rigaku R-Axis RAPID Imaging
 Plate diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.009$, $T_{\max} = 0.982$
 6710 measured reflections

1089 independent reflections
 711 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.246$
 $\theta_{\max} = 68.2^\circ$
 $h = -4 \rightarrow 4$
 $k = -6 \rightarrow 6$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.241$
 $wR(F^2) = 0.565$
 $S = 1.78$
 1089 reflections
 100 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + \{0.187[\text{Max}(F_o^2, 0) + 2F_c^2]/3\}^2]$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.60$ e Å⁻³
 $\Delta\rho_{\min} = -1.40$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C8	1.240 (10)	C6—C7	1.37 (1)
N2—C6	1.42 (1)	C7—C7 ⁱ	1.43 (2)
N2—C8	1.367 (10)	C7—C8 ⁱ	1.48 (1)
C6—N2—C8	113.8 (6)	C6—C7—C7 ⁱ	111.3 (9)
C2—C1—C6	123.5 (8)	C6—C7—C8 ⁱ	142.8 (8)
C5—C1—C6	120.1 (7)	C7 ⁱ —C7—C8 ⁱ	105.9 (8)
N2—C6—C1	122.4 (7)	O1—C8—N2	125.4 (7)
N2—C6—C7	104.8 (7)	O1—C8—C7 ⁱ	130.4 (7)
C1—C6—C7	132.7 (8)	N2—C8—C7 ⁱ	104.2 (6)

Symmetry code: (i) 1 - x, 1 - y, 1 - z.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2—H1...O1 ⁱⁱ	0.95	1.92	2.847 (8)	164

Symmetry code: (ii) 2 - x, 2 - y, 1 - z.

All H atoms were positioned geometrically (C—H = 0.95 Å) and refined in the riding-model approximation, with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. In general, it is quite difficult to grow single crystals of good organic pigments because these are insoluble in organic solvents. The single-crystal of DPPP used was extremely small and curved. This resulted in a higher *R* factor than normal. However, the reduced precision does not seriously affect the molecular skeleton and molecular

arrangement. Therefore, the present result provides valuable information about the N atom of the pyridyl ring, whether it remains free (*i.e.* unbonded) or participates in the formation of intermolecular hydrogen bonds. The highest electron-density peak is located 0.12 Å from atom N2 in the final difference Fourier and the deepest hole is located 8.7 Å from atom N1 and 8.9 Å from C4.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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