

3,6-Di-4-pyridylpyrrolo[3,4-c]pyrrole-  
1,4(2H,5H)-dioneJin Mizuguchi,\* Tomohiko Imoda  
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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 = 10.9For 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  $\text{H}_2$  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  $[\bar{1}\bar{1}0]$  alternately. The molecules are stacked in a 'hunter's fence' (*viz.* when viewed from the side, molecules, slipped by  $45^\circ$  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  $\text{H}_2$  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.

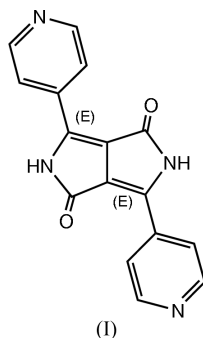
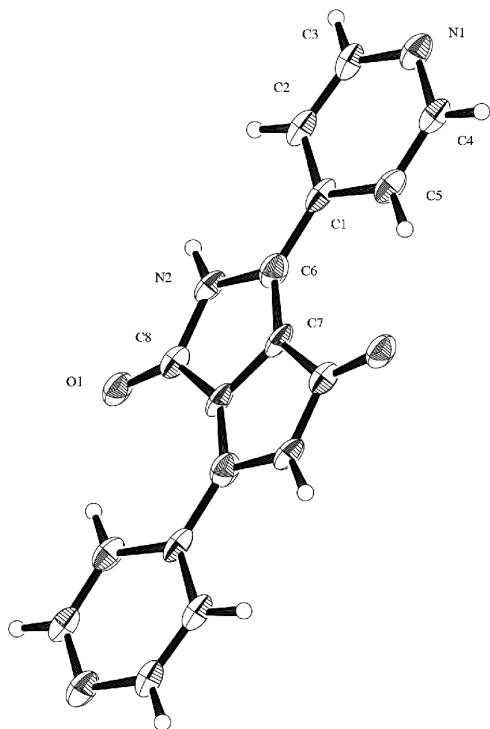


Fig. 1 shows the molecular structure of (I). The molecule is centrosymmetric but not entirely planar; the angle between each pyridyl ring and the central heterocyclic ring system is



**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  $(1-x, 1-y, 1-z)$ .

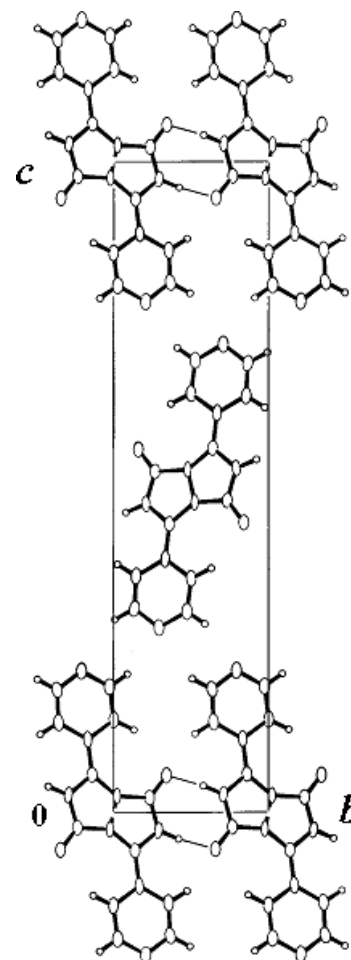
$6.4(3)^\circ$  (Table 1). Fig. 2 shows the projection of the structure on to the  $bc$  plane. The  $p$ -DPPP molecules are connected by  $N-H\cdots O$  bifurcated hydrogen bonds to form a ribbon structure along  $[110]$  and  $[\bar{1}\bar{1}0]$  alternately (Table 2). It is apparent that there are 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  $0.40 \text{ \AA}$  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.

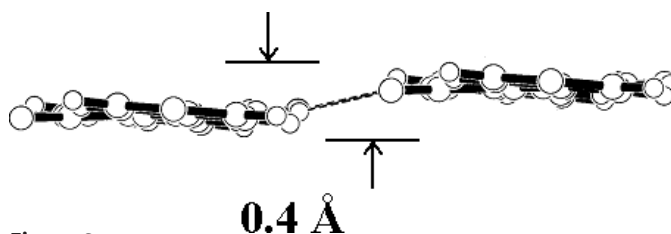
### Crystal data

$C_{16}H_{10}N_4O_2$	$D_x = 1.565 \text{ Mg m}^{-3}$
$M_r = 290.28$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4967 reflections
$a = 3.722(1) \text{ \AA}$	$\theta = 3.3\text{--}68.3^\circ$
$b = 6.263(3) \text{ \AA}$	$\mu = 0.89 \text{ mm}^{-1}$
$c = 26.506(9) \text{ \AA}$	$T = 93.2 \text{ K}$
$\beta = 94.41(2)^\circ$	Platelet, red
$V = 616.0(4) \text{ \AA}^3$	$0.20 \times 0.10 \times 0.02 \text{ mm}$
$Z = 2$	



**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  $0.4 \text{ \AA}$ .

### Data collection

Rigaku R-Axis RAPID Imaging Plate diffractometer	1089 independent reflections
$\omega$ scans	711 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.246$
$T_{\text{min}} = 0.009$ , $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 68.2^\circ$
6710 measured reflections	$h = -4 \rightarrow 4$
	$k = -6 \rightarrow 6$
	$l = -31 \rightarrow 31$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.241$	$w = 1/[\sigma^2(F_o^2) + \{0.187[\text{Max}(F_o^2, 0) + 2F_o^2/3]^2]$
$wR(F^2) = 0.565$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.78$	$\Delta\rho_{\text{max}} = 1.60 \text{ e \AA}^{-3}$
1089 reflections	$\Delta\rho_{\text{min}} = -1.40 \text{ e \AA}^{-3}$
100 parameters	

**Table 1**

Selected geometric parameters (Å, °).

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

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H1 <sup>ii</sup> ···O1 <sup>ii</sup>	0.95	1.92	2.847 (8)	164

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

All H atoms were positioned geometrically ( $C-H = 0.95 \text{ \AA}$ ) and refined in the riding-model approximation, with  $U_{iso} = 1.2U_{eq}(C)$ . 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  $0.12 \text{ \AA}$  from atom N2 in the final difference Fourier and the deepest hole is located  $8.7 \text{ \AA}$  from atom N1 and  $8.9 \text{ \AA}$  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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