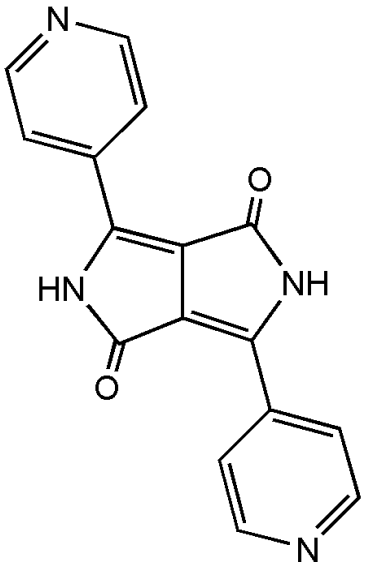
Appendix I

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

para-DPP: phase I

Abstract

The centrosymmetric title compound, $C_{16}H_{10}N_4O_2$, is an organic red pigment utilized for H_2 gas sensors. The centrosymmetric diketopyrrolopyrrole moieties are connected by bifurcated N-H···O hydrogen bonds to form a ribbon structure along [110] and [110] 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.



(I)

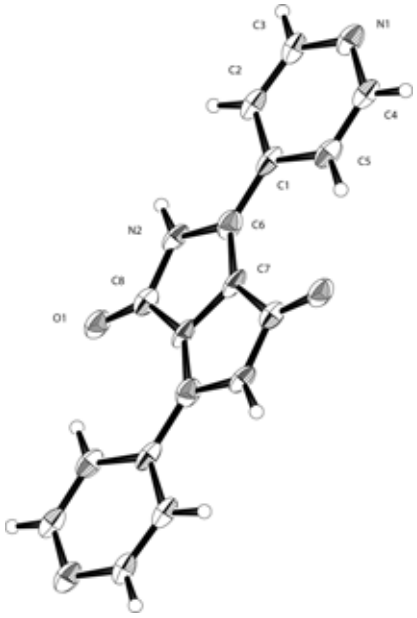


Figure 1

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*).

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 N-H···O intermolecular hydrogen bonds (between the NH group of one molecule and the carbonyl O atom of the neighboring one) and two N-H···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 N-H···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 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···O bifurcated hydrogen bonds to form a ribbon structure along [110] and [110] alternately (Table 2). It is apparent that there are no N-H··· 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

$C_{16}H_{10}N_4O_2$	Dx = 1.565 Mg m^{-3}
Mr = 290.28	Cu $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 4967 reflections
a = 3.722 (1) Å	
b = 6.263 (3) Å	θ = 3.3-68.3°
c = 26.506 (9) Å	μ = 0.89 mm^{-1}
β = 94.41 (2) °	T = 93.2 K
V = 616.0 (4) Å	Platelet, red
Z = 2	0.20 × 0.10 × 0.02 mm

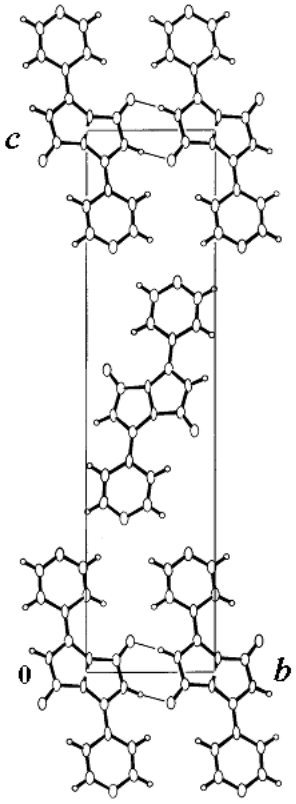


Figure 2

Projection on to the *bc* plane, showing N-H···O intermolecular hydrogen bonds as thin lines.

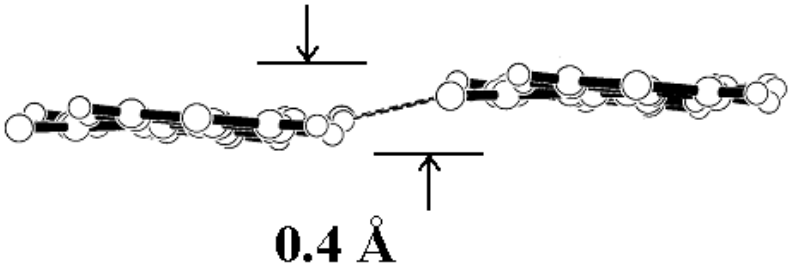


Figure 3

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

Data collection

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

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.241$	$w = 1/[\_2(F_o^2) + \{0.187[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$wR(F^2) = 0.565$	
$S = 1.78$	$(\Delta/\sigma)\mathrm{max} < 0.001$
1089 reflections	$\Delta\rho_{max} = 1.60$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -1.40$ 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)	C7i-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, °).

D-H···A	D-H	H···A	D···A	D-H···A
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_{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 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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