

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

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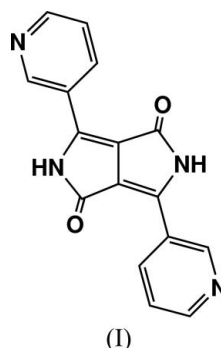
## Key indicators

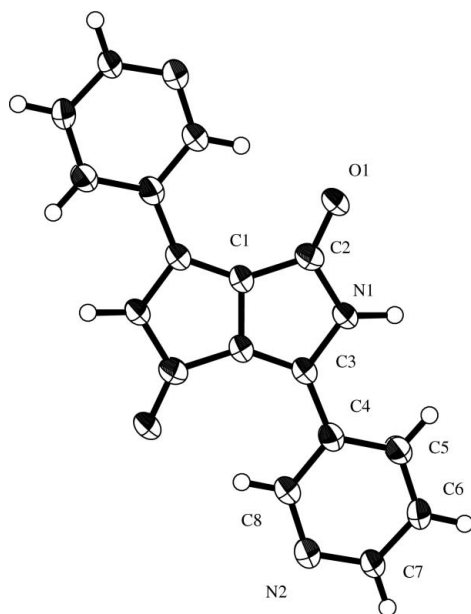
Single-crystal X-ray study  
 $T = 100\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.068  
 $wR$  factor = 0.213  
Data-to-parameter ratio = 10.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$ , is an organic red pigment utilized for hydrogen gas sensors. The centrosymmetric diketopyrrolopyrrole is nearly planar and is linked to four neighbouring molecules *via*  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds to form a two-dimensional network in the (201) plane.

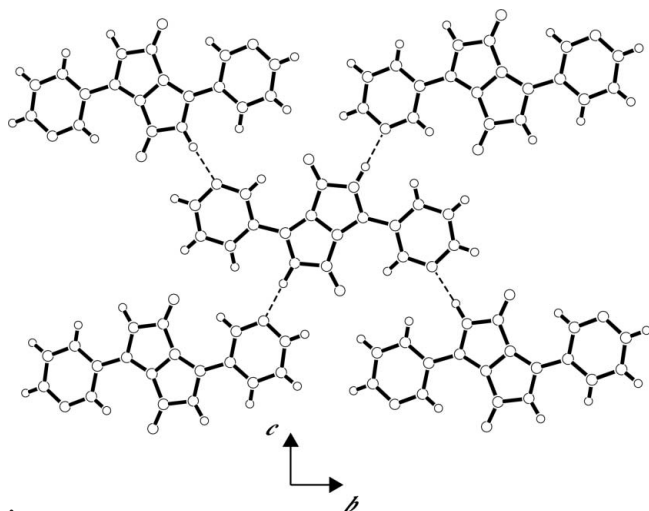
## Comment

Diketodiphenylpyrrolopyrroles are industrially important red pigments (Herbst & Hunger, 1993). The title compound (*m*-DPPP) is a dipyridyl derivative whose N atom of the pyridyl ring is located at the *meta*-site. There are also *o*- and *p*-derivatives. Among these, only *p*-DPPP was found to exhibit a high proton affinity due to the N atom of the pyridyl ring (Mizuguchi, 1993). Because of this, *p*-DPPP has recently attracted attention as a high-performance hydrogen gas sensor (Takahashi & Mizuguchi, 2005). In phase I of *p*-DPPP, there are  $\text{N}-\text{H}\cdots\text{O}$  bifurcated hydrogen bonds between the NH group of one molecule and the O atom of a neighbouring one, and the two N atoms of the pyridyl rings remain free (*i.e.* unbonded) to accept protons, as is necessary for hydrogen gas sensors (Mizuguchi *et al.*, 2005). Phase II of *p*-DPPP is rather insensitive to protons because one N atom of the two pyridyl rings is blocked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds (Mizuguchi *et al.*, 2002). Quite recently, we have also carried out the structure analysis of *o*-DPPP in order to explain its poor sensitivity to protons (Imoda *et al.*, 2005). We found that there are  $\text{N}-\text{H}\cdots\text{N}$  bifurcated hydrogen bonds between the NH group of one molecule and the N atom of the pyridyl ring of a neighbouring one where one molecule is bonded to two neighbouring molecules through four  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds. Therefore, the N atom of the pyridyl ring required as proton acceptor is totally blocked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds and thus quite insensitive to protons. The purpose of the present investigation is to analyze the crystal structure of *m*-DPPP in order to clarify why this compound is insensitive to protons.

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**Figure 1**  
A view of the molecular structure of (I), showing 50% probability displacement ellipsoids for non-H atoms. The unlabeled atoms are related to the labeled ones by the symmetry code  $(1 - x, 1 - y, 1 - z)$ .



**Figure 2**  
Molecular arrangement, showing N—H...N intermolecular hydrogen bonds as dashed lines. One molecule is hydrogen-bonded to four different molecules in the (201) plane.

Fig. 1 shows an *ORTEP* (Burnett *et al.*, 1996) plot of the centrosymmetric *m*-DPPP, (I). The central heterocyclic ring system is planar, as shown by the dihedral angle of  $0.1(2)^\circ$  between the least-squares planes of the heterocyclic five-membered rings. The pyridyl rings are slightly rotated from the central ring system by  $3.6(1)^\circ$ . As shown in Fig. 2, one molecule is bonded to four neighbouring molecules through N—H...N hydrogen bonds (Table 2). This constitutes a two-dimensional network in the (201) plane. The present hydrogen-bond network is strikingly different from those of phases I and II of *p*-DPPP and also from that of *o*-DPPP. In addition, it should be noted that, in the crystal structures of ordinary pyrrolopyrrole pigments without any pyridyl rings,

the molecule is bonded to two molecules through four bifurcated N—H...O hydrogen bonds (Mizuguchi, 2000). As is evident from Fig. 2, the N atom of the pyridyl ring is totally blocked by the N—H...N bonds. This indicates that *m*-DPPP is quite insensitive to protons.

## Experimental

*m*-DPPP was synthesized according to the method reported previously (Rochat *et al.*, 1986) and purified three times by sublimation, using a two-zone furnace (Mizuguchi, 1981). Crystals of *m*-DPPP were dissolved in dimethylformamide at 423 K in an autoclave and crystallized with a cooling rate of  $2 \text{ K h}^{-1}$ . A number of needle-like crystals were obtained. However, these crystals were extremely small.

### Crystal data

$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$   
 $M_r = 290.28$   
 Monoclinic,  $P2_1/c$   
 $a = 3.6616(5) \text{ \AA}$   
 $b = 15.0089(19) \text{ \AA}$   
 $c = 10.9791(13) \text{ \AA}$   
 $\beta = 98.823(9)^\circ$   
 $V = 596.23(13) \text{ \AA}^3$   
 $Z = 2$

$D_x = 1.617 \text{ Mg m}^{-3}$   
 Cu  $K\alpha$  radiation  
 Cell parameters from 4298 reflections  
 $\theta = 4.1\text{--}68.2^\circ$   
 $\mu = 0.92 \text{ mm}^{-1}$   
 $T = 100.1 \text{ K}$   
 Needle, red  
 $0.10 \times 0.03 \times 0.02 \text{ mm}$

### Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)  
 $T_{\text{min}} = 0.896$ ,  $T_{\text{max}} = 0.982$   
 6375 measured reflections

1097 independent reflections  
 520 reflections with  $F^2 > 2\sigma(F^2)$   
 $R_{\text{int}} = 0.109$   
 $\theta_{\text{max}} = 68.2^\circ$   
 $h = -4 \rightarrow 4$   
 $k = -18 \rightarrow 18$   
 $l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.213$   
 $S = 1.03$   
 1097 reflections  
 105 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0947P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O1—C2	1.235 (4)	C1—C2	1.460 (5)
N1—C2	1.406 (5)	C1—C3 <sup>i</sup>	1.372 (5)
N1—C3	1.396 (5)	C3—C4	1.459 (5)
C1—C1 <sup>i</sup>	1.417 (5)		
C2—N1—C3	112.1 (3)	N1—C2—C1	103.7 (3)
C1 <sup>i</sup> —C1—C2	107.7 (3)	N1—C3—C1 <sup>i</sup>	106.9 (3)
C1 <sup>i</sup> —C1—C3 <sup>i</sup>	109.6 (3)	N1—C3—C4	121.1 (3)
C2—C1—C3 <sup>i</sup>	142.7 (3)	C1 <sup>i</sup> —C3—C4	132.0 (3)
O1—C2—N1	123.2 (3)	C3—C4—C5	123.6 (3)
O1—C2—C1	133.2 (4)	C3—C4—C8	118.3 (3)

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

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N1—H1N...N2 <sup>ii</sup>	1.02 (4)	1.93 (4)	2.939 (4)	168 (3)

Symmetry code: (ii)  $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$ .

The H atom of the NH group was found in a difference map and refined isotropically. All other H atoms were positioned geometrically and included in the riding-model approximation, with C—H distances of 0.95 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2005); program(s) used to solve structure: *SIR2002* (Burla *et al.*, 2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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