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3,6-Di-2-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 $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.091
 wR factor = 0.346
Data-to-parameter ratio = 10.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.3,6-Di-2-pyridylpyrrolo[3,4-*c*]pyrrole-
1,4(2*H*,5*H*)-dione

The 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 asymmetric unit contains two half-molecules, each molecule being centrosymmetric. The two independent centrosymmetric diketopyrrolopyrrole moieties are connected by $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds to form a ribbon structure along [100]. The molecules are stacked in a 'hunter's fence' fashion (*viz.* when viewed from the side, molecules, slipped by about 70° within molecular stacks, cross each other in a fence-like structure) along the b axis.

Comment

Diketodiphenylpyrrolopyrroles are industrially important red pigments (Herbst & Hunger, 1993). The title compound, (I) (*o*-DPPP), is a dipyridyl derivative whose N atom of the pyridyl ring is located at the *ortho* site. There are also *meta* and *para* 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 H_2 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 the neighboring one and the two N atoms of the pyridyl rings remain free (*i.e.* unbonded) to accept protons necessary for H_2 gas sensors (Mizuguchi *et al.*, 2005). There is also phase II of *p*-DPPP which 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). The purpose of the present investigation was to analyze the crystal structure of *o*-DPPP in order to account for its poor sensitivity to protons.

There are two independent half-molecules *A* and *B* in the asymmetric unit (Fig. 1). Molecules *A* and *B* are centrosymmetric but not entirely planar. The angles between each pyridyl ring and the heterocyclic ring systems are $10.9(2)^\circ$ in molecule *A* and $1.8(2)^\circ$ in molecule *B*. As shown in Fig. 2, there are $\text{N}-\text{H}\cdots\text{N}$ intermolecular hydrogen bonds (Table 2). There are chains of $\text{N}-\text{H}\cdots\text{N}$ intermolecular hydrogen bonds

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Figure 1

A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. The unlabeled atoms in molecules A and B are related by the symmetry codes $(1 - x, 2 - y, 1 - z)$ and $(1 - x, 1 - y, 1 - z)$, respectively.

between the NH group of one molecule and the N of the pyridyl ring of the neighboring one along the *a* axis. However there are two kinds of chains; one is composed of only molecule A and one of only molecule B. This are designated A and B in Fig. 2. Fig. 3 is the projection on to the *bc* plane, showing how molecules A and B are differently stacked along the *b* axis.

Experimental

o-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 *o*-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.

Crystal data

$C_{16}H_{10}N_4O_2$	$D_x = 1.587 \text{ Mg m}^{-3}$
$M_r = 290.28$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/a$	Cell parameters from 9840 reflections
$a = 16.097(2) \text{ \AA}$	$\theta = 2.9\text{--}68.4^\circ$
$b = 3.7144(5) \text{ \AA}$	$\mu = 0.90 \text{ mm}^{-1}$
$c = 21.725(2) \text{ \AA}$	$T = 93.2 \text{ K}$
$\beta = 110.758(7)^\circ$	Platelet, red
$V = 1214.6(3) \text{ \AA}^3$	$0.60 \times 0.20 \times 0.20 \text{ mm}$
$Z = 4$	

Data collection

Rigaku R-Axis RAPID Imaging Plate diffractometer	2028 independent reflections
ω scans	1647 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (Higashi, 1995)	$R_{\text{int}} = 0.079$
$T_{\text{min}} = 0.292$, $T_{\text{max}} = 0.835$	$\theta_{\text{max}} = 68.3^\circ$
9996 measured reflections	$h = -19 \rightarrow 19$
	$k = -3 \rightarrow 3$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.091$	$w = 1/[\sigma^2(F_o^2) + \{0.149[\text{Max}(F_o^2, 0) + 2F_c^2/3]\}^2]$
$wR(F^2) = 0.346$	$(\Delta/\sigma)_{\text{max}} = 0.012$
$S = 1.91$	$\Delta\rho_{\text{max}} = 0.68 \text{ e \AA}^{-3}$
2028 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
199 parameters

Figure 2

Molecular arrangement of (I), showing N—H...N intermolecular hydrogen bonds as dotted lines.

Table 1

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

O1—C2	1.228 (6)	C1—C2	1.464 (7)
O2—C10	1.226 (6)	C1—C3 ⁱ	1.375 (7)
N1—C2	1.412 (6)	C3—C4	1.460 (7)
N1—C3	1.383 (6)	C9—C9 ⁱⁱ	1.422 (8)
N3—C10	1.402 (6)	C9—C10	1.465 (6)
N3—C11	1.373 (6)	C9—C11 ⁱⁱ	1.390 (7)
C1—C1 ⁱ	1.420 (8)	C11—C12	1.457 (6)
C2—N1—C3	111.6 (4)	C1 ⁱ —C3—C4	130.7 (4)
C10—N3—C11	113.0 (4)	C9 ⁱⁱ —C9—C10	108.1 (5)
C1 ⁱ —C1—C2	107.8 (5)	C9 ⁱⁱ —C9—C11 ⁱⁱ	108.2 (5)
C1 ⁱ —C1—C3 ⁱ	108.8 (5)	C10—C9—C11 ⁱⁱ	143.6 (4)
C2—C1—C3 ⁱ	143.4 (4)	O2—C10—N3	124.6 (4)
O1—C2—N1	124.6 (4)	O2—C10—C9	132.2 (4)
O1—C2—C1	131.7 (4)	N3—C10—C9	103.2 (4)
N1—C2—C1	103.7 (4)	N3—C11—C9 ⁱⁱ	107.5 (4)
N1—C3—C1 ⁱ	108.1 (4)	N3—C11—C12	122.3 (4)
N1—C3—C4	121.1 (4)	C9 ⁱⁱ —C11—C12	130.2 (4)

Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$.

Table 2

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1—H1 $\cdots$ N2 ⁱⁱⁱ	0.95	2.19	3.099 (6)	159
N3—H2 $\cdots$ N4 ^{iv}	0.95	2.22	3.120 (6)	159

Symmetry codes: (iii) $\frac{1}{2} - x, y, 1 - z$; (iv) $\frac{1}{2} - x, y, -z$.

All H atoms were positioned geometrically ($C\text{—}H = 0.95 \text{ \AA}$) and included in the riding-model approximation, with $U_{\text{iso}} = 1.2U_{\text{eq}}(C)$. In most crystals, there are tiny cracks along the long crystal axis, presumably accounts for the higher than normal *R* factor.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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Figure 3
Projection of the structure of (I) on to the *bc* plane.

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