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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 K
Mean σ(C–C) = 0.007 Å
R factor = 0.091
wR factor = 0.346
Data-to-parameter ratio = 10.2

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

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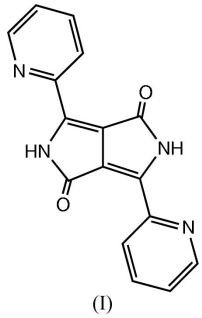
The title compound, $C_{16}H_{10}N_4O_2$, is an organic red pigment utilized for H_2 gas sensors. The asymmetric unit contains two half-molecules, each molecule being centrosymmetric. The two independent centrosymmetric diketopyrrolopyrrole moieties are connected by N—H···N hydrogen bonds to form a ribbon structure along [100]. The molecules are stacked in a 'hunter's fence' fashion (*viz.* when viewed from the side, molecles, slipped by about 70° within moleclar 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 N—H···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 N—H···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.



(I)

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)° in molecule *A* and 1.8 (2)° in molecule *B*. As shown in Fig. 2, there are N—H···N intermolecular hydrogen bonds (Table 2). There are chains of N—H···N intermolecular hydrogen bonds

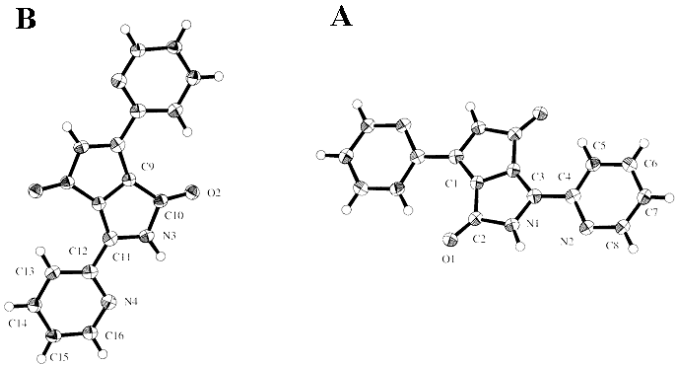


Figure 1
A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. The unlabeled atoms in molecules *A* and *B* are related by the symmetry codes $(1-x, 2-y, 1-z)$ and $(1-x, 1-y, 1-z)$, respectively.

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

$C_{16}H_{10}N_4O_2$
$M_r = 290.28$
Monoclinic, $P2/a$
$a = 16.097\ (2)$ Å
$b = 3.7144\ (5)$ Å
$c = 21.725\ (2)$ Å
$\beta = 110.758\ (7)^\circ$
$V = 1214.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.587$ Mg m^{-3}
Cu Kα radiation
Cell parameters from 9840 reflections
$\theta = 2.9$–68.4°
$\mu = 0.90$ mm^{-1}
$T = 93.2$ K
Platelet, red
0.60 × 0.20 × 0.20 mm

Data collection

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

Refinement

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

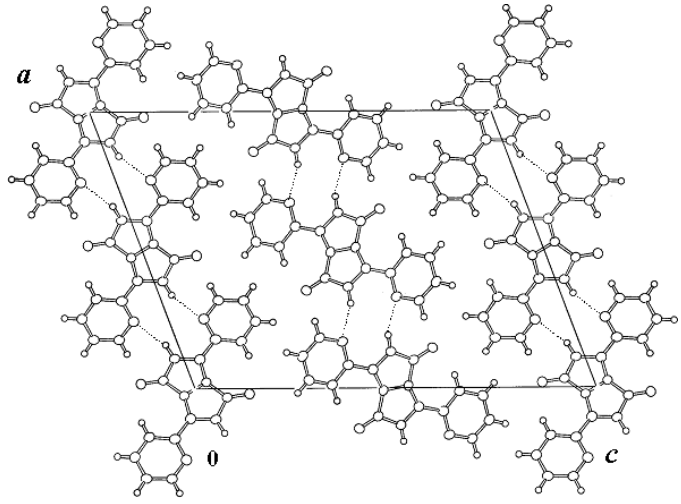


Figure 2
Molecular arrangement of (I), showing N—H···N intermolecular hydrogen bonds as dotted lines.

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2^{iii}	0.95	2.19	3.099 (6)	159
N3—H2···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—H = 0.95 Å) and included in the riding-model approximation, with $U_{iso} = 1.2U_{eq}$(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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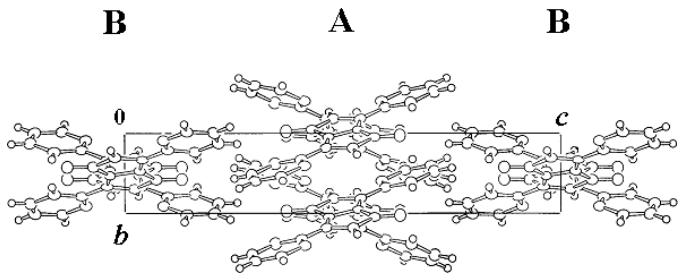

Figure 3
Projection of the structure of (I) on to the *bc* plane.

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