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

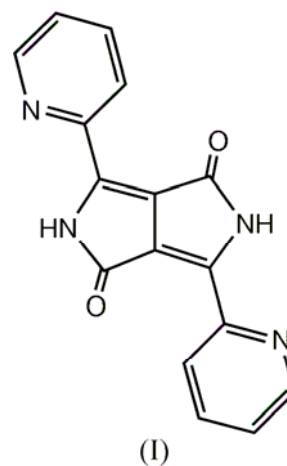***ortho*-DPPP: Phase I**

Abstract

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, 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 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

(I)

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)° 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 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.
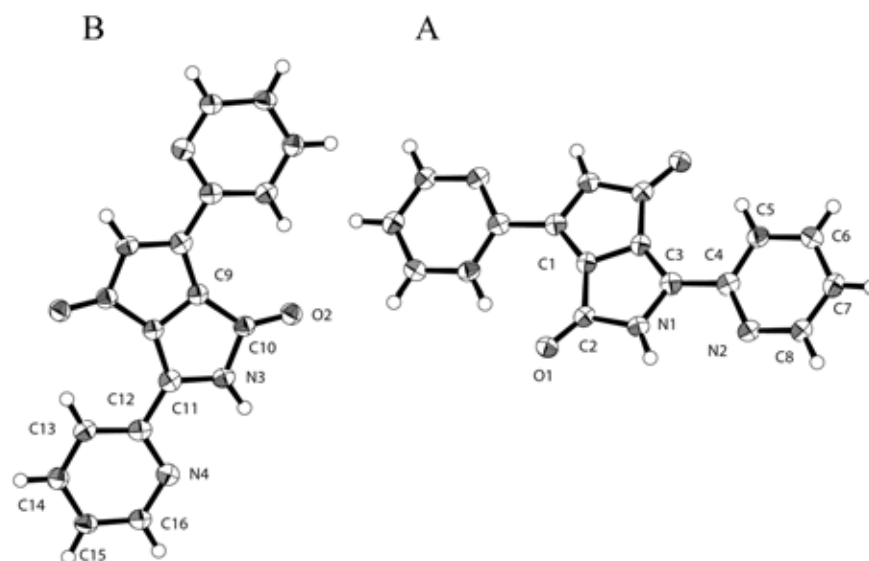

Figure 1

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.

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.
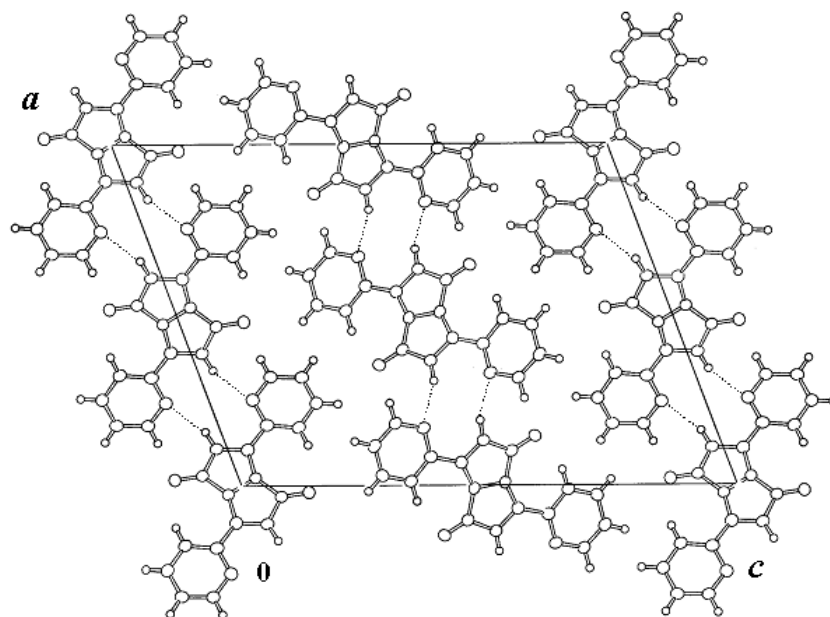
Figure 2

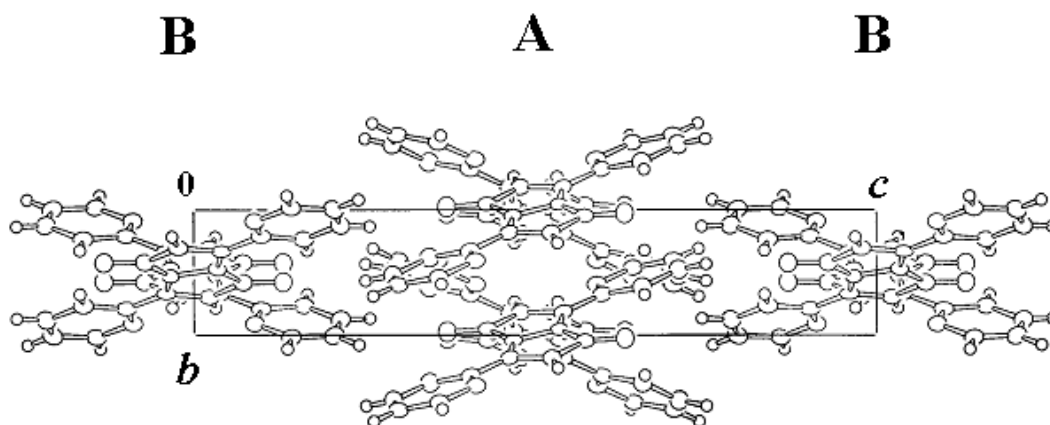Molecular arrangement of (I), showing N—H⋯N intermolecular hydrogen bonds as dotted lines.

Figure 3

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

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)°

$V = 1214.6$ (3) Å^3

$Z = 4$

$D_x = 1.587$ Mg m^{-3}

Cu $K\alpha$ radiation

Cell parameters from 9840 reflections

$\theta = 2.9$–68.4°

$\mu = 0.90$ mm^{-1}

$T = 93.2$ K

Platelet, red

$0.60 \times 0.20 \times 0.20$ 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)

$R_{int} = 0.079$

$\theta_{max} = 68.3°$

$h = -19 \to 19$

$k = -3 \to 3$

$l = -25 \to 25$

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

$w = 1/[\sigma^2(F_o^2) + \{0.149[\text{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$

$(\Delta/\sigma)\text{max} = 0.012$

$\Delta\rho_{max} = 0.68$ e Å^{-3}

$\Delta\rho_{min} = -0.47$ e Å^{-3}

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) 1/2 - x; y; 1 - z; (iv) 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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