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

The title compound, C_{16}H_{10}N_{4}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 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 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. These 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

$C_{16}H_{10}N_{4}O_{2}$

$M_r = 290.28$

Monoclinic, $P2_1/a$

$a = 16.097 (2) \AA$

$b = 3.7144 (5) \AA$

$c = 21.725 (2) \AA$

$\beta = 110.758 (7)^\circ$

$V = 1214.6 (3) \AA^3$

$Z = 4$

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer

$\omega$ scans

Absorption correction: multi-scan (Higashi, 1995)

$T_{\text{max}} = 0.292$, $T_{\text{min}} = 0.835$

9996 measured reflections

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

$w = 1/[\sigma^2(F^2) + (0.149\max(F^2))^2 + 2F^2]^3$

$\Delta/\sigma = 0.012$

$\Delta_{\text{max}} = 0.68 \text{ e} \AA^{-3}$

$\Delta_{\text{min}} = -0.47 \text{ e} \AA^{-3}$

//

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.

Figure 1

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

Table 1

<table>
<thead>
<tr>
<th></th>
<th>D—H···A</th>
<th>D—H···A</th>
<th>D···A</th>
<th>D···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1—H1···N2</td>
<td>0.95</td>
<td>2.19</td>
<td>3.099 (6)</td>
<td>159</td>
</tr>
<tr>
<td>N3—H2···N4</td>
<td>0.95</td>
<td>2.22</td>
<td>3.120 (6)</td>
<td>159</td>
</tr>
</tbody>
</table>

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

All H atoms were positioned geometrically (C—H = 0.95 Å) and included in the riding-model approximation, with $U_{	ext{iso}} = 1.2U_{	ext{eq}}$(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.
References

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