Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: **W. Clegg** and **D. G. Watson**

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

Tsuyoshi Hirota, Tomohiko Imoda, Hiroo Takahashi and Jin Mizuguchi

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site provided that this cover page is retained. Republication of this article or its storage in electronic databases or the like is not permitted without prior permission in writing from the IUCr.

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

Tsuyoshi Hirota, Tomohiko Imoda, Hiroo Takahashi and Jin Mizuguchi*

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

Correspondence e-mail: mizu-j@ynu.ac.jp

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 = 10.4

For 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.

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 K h^{-1} . A number of needle-like crystals were obtained. However, these crystals were extremely small.

Crystal data

$\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2$	$D_x = 1.617 \text{ Mg m}^{-3}$
$M_r = 290.28$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 4298 reflections
$a = 3.6616(5) \text{ \AA}$	$\theta = 4.1\text{--}68.2^\circ$
$b = 15.0089(19) \text{ \AA}$	$\mu = 0.92 \text{ mm}^{-1}$
$c = 10.9791(13) \text{ \AA}$	$T = 100.1 \text{ K}$
$\beta = 98.823(9)^\circ$	Needle, red
$V = 596.23(13) \text{ \AA}^3$	$0.10 \times 0.03 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Rigaku R-Axis RAPID imaging-plate diffractometer	1097 independent reflections
ω scans	520 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	$R_{\text{int}} = 0.109$
$T_{\text{min}} = 0.896$, $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 68.2^\circ$
6375 measured reflections	$h = -4 \rightarrow 4$
	$k = -18 \rightarrow 18$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.068$	$w = 1/[\sigma^2(F_o^2) + (0.0947P)^2]$
$wR(F^2) = 0.213$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1097 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
105 parameters	$\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

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 ⁱ	1.372 (5)
N1—C3	1.396 (5)	C3—C4	1.459 (5)
C1—C1 ⁱ	1.417 (5)		
C2—N1—C3	112.1 (3)	N1—C2—C1	103.7 (3)
C1 ⁱ —C1—C2	107.7 (3)	N1—C3—C1 ⁱ	106.9 (3)
C1 ⁱ —C1—C3 ⁱ	109.6 (3)	N1—C3—C4	121.1 (3)
C2—C1—C3 ⁱ	142.7 (3)	C1 ⁱ —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 ⁱⁱ	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/ MSC, 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: *Crystal-Structure*.

The authors express their sincere thanks to Dr S. Suzuki for the preparation of *m*-DPPP.

References

- Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polodori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Herbst, W. & Hunger, K. (1993). *Industrial Organic Pigments*, 2nd ed., pp. 467–475. Weinheim: VCH.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Imoda, T., Hirota, T., Takahashi, H. & Mizuguchi, J. (2005). *Acta Cryst.* **E61**, o616–o618.
- Mizuguchi, J. (1981). *Cryst. Res. Technol.* **16**, 695–700.
- Mizuguchi, J. (1993). *Ber. Bunsenges. Phys. Chem.* **97**, 684–693.
- Mizuguchi, J. (2000). *J. Phys. Chem. A*, **104**, 1817–1821.
- Mizuguchi, J., Imoda, T. & Takahashi, H. (2005). *Acta Cryst.* **E61**, o500–o502.
- Mizuguchi, J., Takahashi, H. & Yamakami, H. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 519–520.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Rigaku/MS (2005). *CrystalStructure*. Version 3.7.0. Rigaku Corporation, Tokyo, Japan.
- Rochat, A. C., Cassar, L. & Iqbal, A. (1986). US Patent 4 579 949.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Takahashi, H. & Mizuguchi, J. (2005). *J. Electrochem. Soc.* **152**, H69–H73.