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N,*N*′-Di-2-pyridylperylene-3,4:9,10-bis(dicarboximide)

Jin Mizuguchi,* Kazuyuki Hino, Kazuyuki Sato, Hiroo Takahashi and Shigeru Suzuki

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

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

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Key indicators

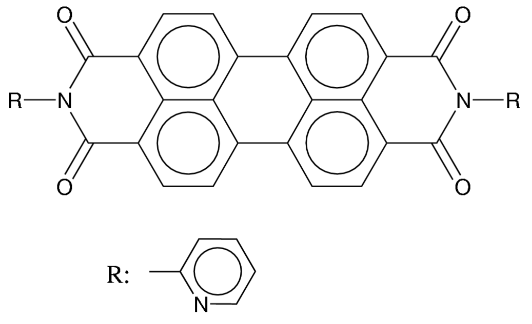
Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.006 Å
R factor = 0.062
wR factor = 0.045
Data-to-parameter ratio = 11.1

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

The title compound, $C_{34}H_{16}N_4O_4$, is a perylene–imide pigment utilized for H_2 gas sensors. There are two independent half-molecules in the asymmetric unit. The symmetry of both molecules is C_i. The angles between the each of the pyridyl rings and the perylene-imide skeleton are 77.7 (1) and 72.8 (1) in the two molecules. The independent molecules are stacked alternately along the *b* axis.

Comment

Perylene compounds are industrially important pigments, covering a variety of shades from red *via* maroon to black (Herbst & Hunger, 1993). The title compound, (I), is an *ortho*-pyridyl derivative, abbreviated to OPP.



(I)

We have carried out a series of investigations on H_2 gas sensors utilizing a high proton affinity of organic pigments that have pyridyl rings connected directly to the choromophore (Takahashi & Mizuguchi, 2005). The N atom of the pyridyl ring works as a strong proton acceptor and plays a decisive role for signal detection. OPP exhibits a resistivity change of about three orders of magnitude even for 0.05% H_2. Other than the present *ortho* derivative, there are also *meta* and *para* derivatives and their sensitivity is slightly different, depending the site of the N atom. In this connection, structure analyses of these derivatives have been carried out. The structures of the *meta* and *para* derivatives are reported in the preceding and following papers, respectively (Mizuguchi *et al.*, 2005; Hino *et al.*, 2005). This paper reports the structure of the *ortho* derivative.

The two independent molecules, *A* and *B*, of OPP (Fig. 1) are characterized by the same molecular C_i symmetry. The molecular conformations of these molecules are quite similar, but the twist angle of the pyridyl rings is different. The angles between each of the pyridyl rings and the perylene-imide

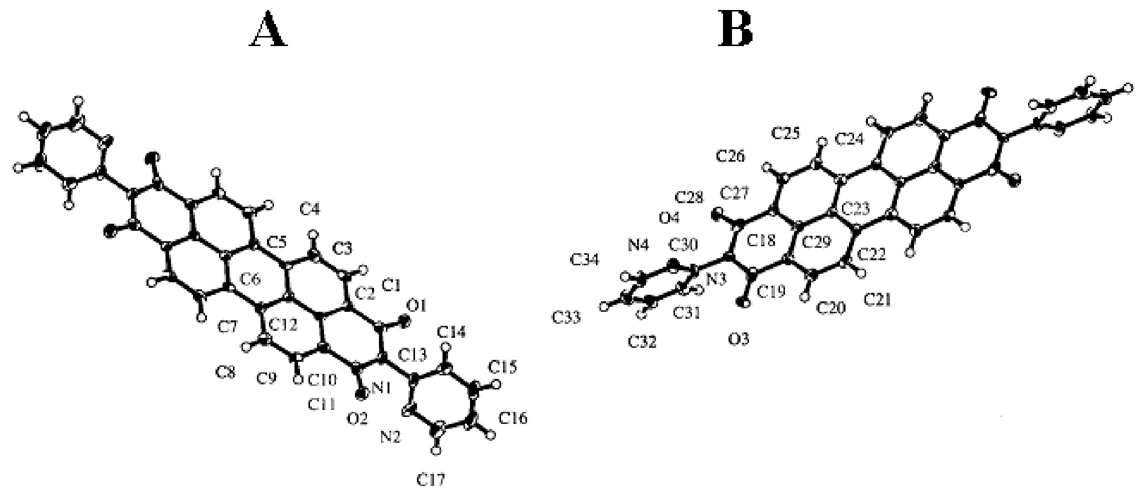


Figure 1
A view of the molecular conformations of the two independent molecules of (I), showing 50% displacement ellipsoids for the non-H atoms. Unlabelled atoms in A are related to labelled atoms by $-x$, $1 - y$, $1 - z$; unlabelled atoms in B are related to labelled atoms by $2 - x$, $1 - y$, $-z$.

skeleton are 77.7 (1)° in molecule *A* and 72.8 (1)° in molecule *B*. The perylene–imide skeleton is planar (r.m.s. deviations = 0.048 and 0.032 Å for the two molecules in the asymmetric unit). Molecules *A* and *B* are stacked alternately along the *b* axis, as shown in Fig. 2.

Experimental

OPP was synthesized by reaction of perylenetetracarboxylic dianhydride with 1,2-di-2-pyridyldiamine in dimethylnaphthalene at 490 K for 3 h according to the method of Herbst & Hunger (1993). The product was then purified three times by sublimation at 760 K, using a two-zone furnace (Mizuguchi, 1981). Single crystals of OPP 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 needles.

Crystal data

$C_{34}H_{16}N_4O_4$
$M_r = 544.51$
Monoclinic, $P2_1/c$
$a = 17.599$ (1) Å
$b = 7.1705$ (5) Å
$c = 20.679$ (2) Å
$\beta = 111.004$ (5)°
$V = 2436.2$ (3) Å^3
$Z = 4$
$D_x = 1.485$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 12013 reflections
$\theta = 3.6$–65.6°
$\mu = 0.82$ mm^{-1}
$T = 93.2$ K
Needle, red
0.50 × 0.09 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\rm min} = 0.960$, $T_{\rm max} = 0.960$
20469 measured reflections
4219 independent reflections
2120 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.051$
$\theta_{\rm max} = 68.2°$
$h = -21 \rightarrow 21$
$k = -7 \rightarrow 7$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.045$
$S = 1.89$
4219 reflections
379 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.47$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.49$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.217 (4)	C8—C9	1.392 (5)
O2—C11	1.202 (4)	C9—C10	1.378 (5)
O3—C18	1.196 (4)	C10—C11	1.494 (5)
O4—C28	1.217 (4)	C10—C12	1.414 (4)
N1—C1	1.422 (4)	C18—C19	1.506 (5)
N1—C11	1.418 (4)	C19—C20	1.377 (5)
N3—C18	1.399 (4)	C19—C29	1.405 (4)
N3—C28	1.434 (4)	C20—C21	1.401 (5)
C1—C2	1.496 (5)	C21—C22	1.390 (4)
C2—C3	1.382 (4)	C22—C23	1.435 (5)
C2—C12	1.417 (4)	C22—C24$^{\rm ii}$	1.480 (5)
C3—C4	1.385 (5)	C23—C24	1.427 (4)
C4—C5	1.401 (5)	C23—C29	1.437 (5)
C5—C6	1.447 (4)	C24—C25	1.393 (5)
C5—C7$^{\rm i}$	1.468 (5)	C25—C26	1.393 (5)
C6—C7	1.437 (5)	C26—C27	1.395 (4)
C6—C12	1.427 (5)	C27—C28	1.487 (5)
C7—C8	1.394 (4)	C27—C29	1.420 (5)
C1—N1—C11	127.6 (4)	C6—C12—C10	119.4 (4)
C18—N3—C28	125.5 (4)	O3—C18—N3	120.9 (4)
O1—C1—N1	121.5 (4)	O3—C18—C19	123.5 (4)
O1—C1—C2	123.8 (4)	N3—C18—C19	115.5 (4)
N1—C1—C2	114.8 (4)	C18—C19—C20	117.8 (4)
C1—C2—C3	118.3 (4)	C18—C19—C29	121.3 (4)
C1—C2—C12	120.5 (4)	C20—C19—C29	120.9 (4)
C3—C2—C12	121.1 (4)	C19—C20—C21	120.1 (4)
C2—C3—C4	120.6 (4)	C20—C21—C22	121.5 (4)
C3—C4—C5	121.0 (4)	C21—C22—C23	119.4 (4)
C4—C5—C6	119.5 (4)	C21—C22—C24$^{\rm ii}$	122.2 (4)
C4—C5—C7$^{\rm i}$	121.9 (4)	C23—C22—C24$^{\rm ii}$	118.4 (4)
C6—C5—C7$^{\rm i}$	118.6 (4)	C22—C23—C24	122.9 (4)
C5—C6—C7	122.8 (4)	C22—C23—C29	118.3 (4)
C5—C6—C12	118.5 (4)	C24—C23—C29	118.8 (4)
C7—C6—C12	118.6 (4)	C22$^{\rm ii}$—C24—C23	118.7 (4)
C5$^{\rm i}$—C7—C6	118.6 (4)	C22$^{\rm ii}$—C24—C25	121.4 (4)
C5$^{\rm i}$—C7—C8	121.7 (4)	C23—C24—C25	119.9 (4)
C6—C7—C8	119.8 (4)	C24—C25—C26	121.3 (4)
C7—C8—C9	120.7 (4)	C25—C26—C27	120.2 (4)
C8—C9—C10	120.9 (4)	C26—C27—C28	119.5 (4)
C9—C10—C11	118.4 (4)	C26—C27—C29	120.4 (4)
C9—C10—C12	120.5 (4)	C28—C27—C29	120.1 (4)
C11—C10—C12	121.1 (4)	O4—C28—N3	120.4 (4)
O2—C11—N1	120.7 (4)	O4—C28—C27	123.3 (4)
O2—C11—C10	125.0 (4)	N3—C28—C27	116.3 (4)
N1—C11—C10	114.3 (4)	C19—C29—C23	119.8 (4)
C2—C12—C6	119.2 (4)	C19—C29—C27	120.8 (4)
C2—C12—C10	121.3 (4)	C23—C29—C27	119.3 (4)

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

o438 Jin Mizuguchi *et al.* • $C_{34}H_{16}N_4O_4$ *Acta Cryst.* (2005). E**61**, o437–o439

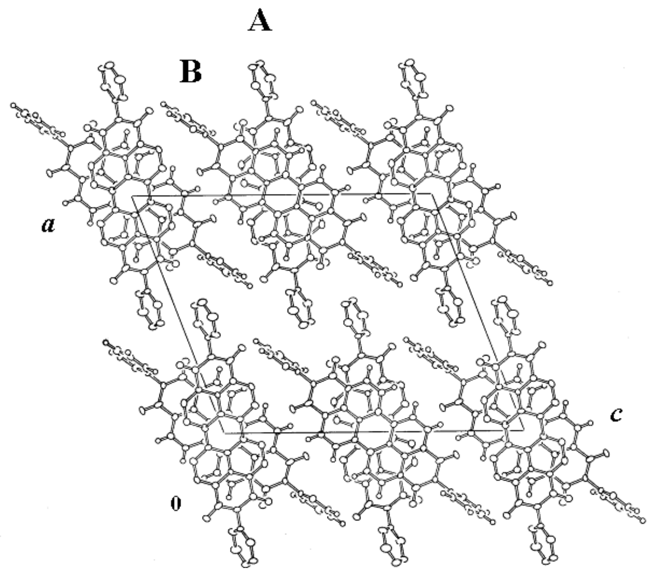


Figure 2
Projection of the structure on to the *ac* plane.

All H atoms were positioned geometrically [C—H = 0.95 Å and $U_{iso} = 1.2U_{eq}(C)$] and refined using a riding model.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); 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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Acta Cryst. (2005). E**61**, o437–o439 Jin Mizuguchi *et al.* • $C_{34}H_{16}N_4O_4$ **o439**