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Key indicators

Single-crystal X-ray study
 T = 93 K
 Mean $\sigma(C-C)$ = 0.007 Å
 Disorder in main residue
 R factor = 0.083
 wR factor = 0.196
 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>.

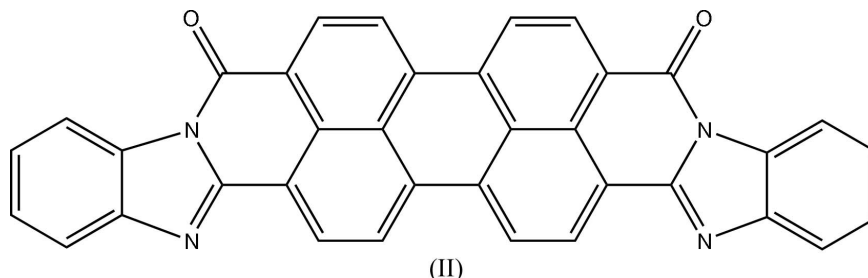
Dibenzimidazo[2,1-a:1',2'-b']anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-6,11-dione: *cis* form (II)

The title compound, $C_{36}H_{16}N_4O_2$, is the *cis* form of a benzimidazole perylene derivative used as a black pigment. The molecule is planar and stacked along the *a* axis. Because of an orientational disorder, a crystallographic center of symmetry appears at the site of the molecule, although the molecule does not have a center of symmetry.

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Comment

Perylene imide compounds are well known organic pigments which exhibit a variety of shades in the range from red *via* maroon to black (Herbst & Hunger, 1993). The title compound, (II), is the *cis* form of a benzimidazoleperylene derivative (abbreviated to BIP) used as a black pigment (Mizuguchi & Shimo, 2005). The background for the present study has been set out in our previous paper (Mizuguchi, 2005), which describes the structure of the *trans* form (I) of BIP.



An *ORTEP* plot (Burnett & Johnson, 1996) of (II) is shown in Fig. 1. The molecule has local C_{2v} symmetry, giving a small dipole moment. The present symmetry is, however, obviously not compatible with the fact that the molecule lies on a center of symmetry. This is due to the orientational disorder of the molecule, as described in the *Experimental* section. The present disordered structure is quite similar to

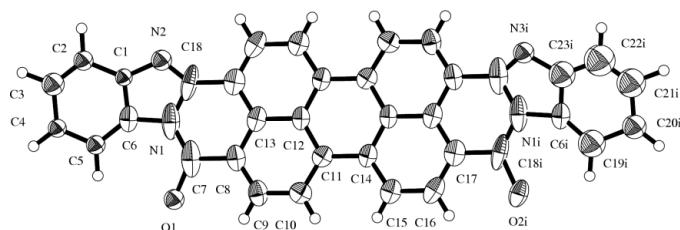


Figure 1
 A view of the molecular structure of (II), showing 50% displacement ellipsoids for non-H atoms. In order to show only one of two possible orientations of the molecule, a set of atoms with 50% site occupancy (O2/N3/C19–C23 and O1ⁱ/N2ⁱ/C1ⁱ–C5ⁱ) have been omitted. [Symmetry code: (i) 1 – x, 1 – y, 2 – z.]

that of the *cis* form of the perinone analog (Mizuguchi, 2003). Fig. 2 shows the projection of the crystal structure along the *a* axis. The molecules are arranged in a zigzag fashion along the *b* axis. Furthermore, the molecules are stacked along the *a* axis.

Experimental

BIP was synthesized by reaction of perylenetetracarboxylic dianhydride with 1,2-phenylenediamine in phenol at 483 K for 6 h (Tamizhmani *et al.*, 1991). The products contained both *trans*-(I) and *cis*-(II) isomers of BIP. The isomers were separated by chromatography using a carrier based on a mixed solvent of trifluoroacetic acid and toluene. The *cis* or *trans* configuration has been confirmed by means of UV-vis solution spectra together with molecular orbital calculations. BIP powders of the *cis* form (II) were purified by sublimation under argon at about 675 K, using a two-zone furnace (Mizuguchi, 1981). Single crystals were then grown from the vapor phase in a closed system at about 650 K. After 48 h, a number of black needle crystals of (II) were obtained.

Crystal data

$C_{36}H_{16}N_4O_2$	$D_x = 1.551 \text{ Mg m}^{-3}$
$M_r = 536.55$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8833 reflections
$a = 4.7501 (6) \text{ \AA}$	$\theta = 3.2\text{--}71.6^\circ$
$b = 28.079 (3) \text{ \AA}$	$\mu = 0.79 \text{ mm}^{-1}$
$c = 8.728 (1) \text{ \AA}$	$T = 93.2 \text{ K}$
$\beta = 99.21 (1)^\circ$	Needle, black
$V = 1149.1 (2) \text{ \AA}^3$	$0.50 \times 0.05 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Rigaku R-Axis RAPID Imaging Plate diffractometer	1969 independent reflections
ω scans	791 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{int} = 0.08$
$T_{min} = 0.727$, $T_{max} = 0.984$	$\theta_{max} = 68.2^\circ$
12407 measured reflections	$h = -4 \rightarrow 4$
	$k = -33 \rightarrow 33$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.083$	$w = 1/[\sigma^2(F_o^2) + \{0.05[\text{Max}(F_o^2, 0) + 2F_c^2/3]\}^2]$
$wR(F^2) = 0.196$	$(\Delta/\sigma)_{max} = 0.009$
$S = 1.14$	$\Delta\rho_{max} = 0.30 \text{ e \AA}^{-3}$
1963 reflections	$\Delta\rho_{min} = -0.25 \text{ e \AA}^{-3}$
188 parameters	

Table 1

Selected geometric parameters (\AA , $^\circ$).

N1—C6	1.374 (6)	N3—C7	1.119 (9)
N1—C7	1.378 (6)	N3—C23	1.43 (1)
N2—C1	1.35 (1)	C1—C6	1.355 (9)
N2—C18	1.16 (1)	C6—C23	1.34 (1)
C10—C11—C14—C15	−2.8 (6)	C11—C14—C15—C16	−178.6 (4)

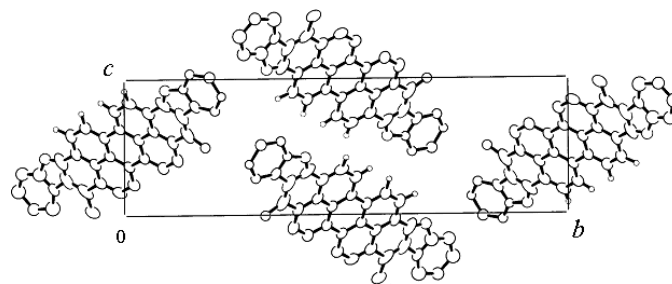


Figure 2

Projection of the crystal structure of (II) along the *a* axis. One of two possible orientations of the molecule has been omitted.

The molecule is disordered in the five-membered ring and at the extremity of the perylene imide skeleton, just as in the case of the *cis* form of the perinone analog (Mizuguchi, 2003). Because of this, a crystallographic center of symmetry appears at the site of the molecule, although the molecule is of the *cis* form. It was assumed that the seven rings around the center of the molecule are not disordered, since they possess a center of symmetry. The terminal part has two possible sets of atoms O1/N2/C1—C5 and O2/N3/C19—C23 with 50% occupancy each, except for atom C6 which is shared. The atoms with occupancy factors of 50% were refined isotropically, except for atom O2 which was refined anisotropically. All H atoms on the perylene imide skeleton were positioned geometrically [$C-H = 0.95 \text{ \AA}$ and $U_{iso}(H) = 1.2U_{eq}(C)$] and not refined. On the other hand, the H atoms attached to the disordered C atoms were also positioned by calculation, but these were shifted slightly during the least-squares refinement, to maintain sensible geometry.

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: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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