

Dibenzimidazo[2,1-a:2',1'-a']anthra-  
[2,1,9-def:6,5,10-d'e'f']diisoquinoline-  
10,21-dione: *trans* form (I)

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

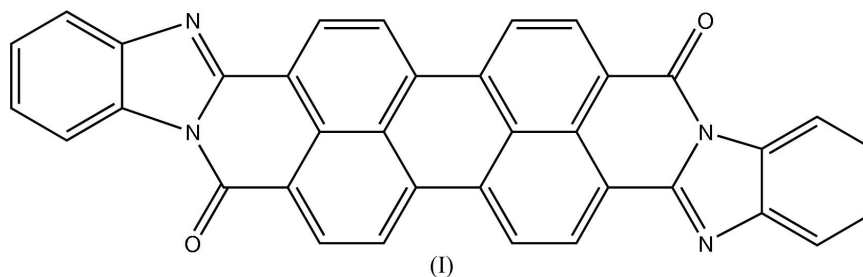
Single-crystal X-ray study  
 $T = 93$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.012$  Å  
 $R$  factor = 0.102  
 $wR$  factor = 0.222  
Data-to-parameter ratio = 9.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{36}\text{H}_{16}\text{N}_4\text{O}_2$ , is the *trans* form of a benzimidazole perylene derivative used as a black pigment. The molecule is entirely planar and possesses a center of symmetry. The molecules are oriented in the same direction and are stacked with a considerable overlap of the perylene imide skeleton along the  $a$  axis.

Received 8 March 2005  
Accepted 14 March 2005  
Online 25 March 2005

## Comment

Perylene and perinone compounds are well known organic pigments which exhibit shades in the range from red to black (Herbst & Hunger, 1993). Both are chemically related. Perylene compounds are derived from perylene-3,4,9,10-tetracarboxylic acid, while perinones are derivatives of naphthalene-1,4,5,8-tetracarboxylic acid. The title compound, (I), is the *trans* form of a benzimidazole perylene derivative (abbreviated to BIP) which has attracted attention as a black pigment (Mizuguchi & Shimo, 2005), as well as an electronic material for electroluminescence (EL) devices (Adachi *et al.*, 1988) and electrophotographic photoreceptors (Loutfy *et al.*, 1989). In perinone analogues of BIP, there are *cis* and *trans* isomers, known as Pigment Orange 43 and Pigment Red 194, on the market, respectively. These structures have recently been reported (Mizuguchi, 2003*a,b*). On the other hand, no structure of BIP has been reported, although the structural information is quite important for electronic applications. The present paper deals with the crystal structure of the *trans* form (I) of BIP while the report on the *cis* form (II) is in the following paper (Mizuguchi, 2005).



The structure of the *trans* form (I) [ $P\bar{1}$ ;  $a = 4.729$  (2) Å,  $b = 8.282$  (2) Å,  $c = 14.693$  (4) Å,  $\alpha = 89.35$  (2)°,  $\beta = 91.15$  (3)° and  $\gamma = 105.83$  (3)°] is similar in most lattice parameters to those of the *cis* form (II) [ $P2_1/c$ ;  $a = 4.7501$  (6) Å,  $b = 28.079$  (3) Å,  $c = 8.728$  (1) Å and  $\beta = 99.21$  (1)°], but the former cell volume is approximately half of the latter. An *ORTEP* plot (Burnett & Johnson, 1996) of (I) is shown in Fig. 1. The molecule is entirely planar and possesses a center of symmetry. All molecules are oriented in the same direction and are stacked with

a considerable overlap of the perylene imide skeleton along the *a* axis, as shown in Fig. 2.

## 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 1:5 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 *trans* form (I) 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 680 K. After 48 h, a number of black needle-shaped crystals of (I) were obtained, but these were slightly curved.

### Crystal data

$C_{36}H_{16}N_4O_2$	$Z = 1$
$M_r = 536.53$	$D_x = 1.602 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Cu $K\alpha$ radiation
$a = 4.729 (2) \text{ \AA}$	Cell parameters from 3329 reflections
$b = 8.282 (2) \text{ \AA}$	$\theta = 3.0\text{--}68.2^\circ$
$c = 14.693 (4) \text{ \AA}$	$\mu = 0.82 \text{ mm}^{-1}$
$\alpha = 89.35 (2)^\circ$	$T = 93.2 \text{ K}$
$\beta = 91.15 (3)^\circ$	Needle, black
$\gamma = 104.83 (3)^\circ$	$0.40 \times 0.05 \times 0.05 \text{ mm}$
$V = 556.2 (3) \text{ \AA}^3$	

### Data collection

Rigaku R-AXIS RAPID Imaging Plate diffractometer	1831 independent reflections
$\omega$ scans	505 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	$R_{\text{int}} = 0.106$
$T_{\text{min}} = 0.490$ , $T_{\text{max}} = 0.960$	$\theta_{\text{max}} = 68.2^\circ$
5005 measured reflections	$h = -4 \rightarrow 4$
	$k = -9 \rightarrow 9$
	$l = -17 \rightarrow 17$

### Refinement

Refinement on $F^2$	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.102$	$w = 1/[\sigma^2(F_o^2) + \{0.042[\max(F_o^2, 0) + 2F_c^2]/3\}^2]$
$wR(F^2) = 0.222$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.93$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
1804 reflections	$\Delta\rho_{\text{min}} = -0.41 \text{ e \AA}^{-3}$
190 parameters	

**Table 1**

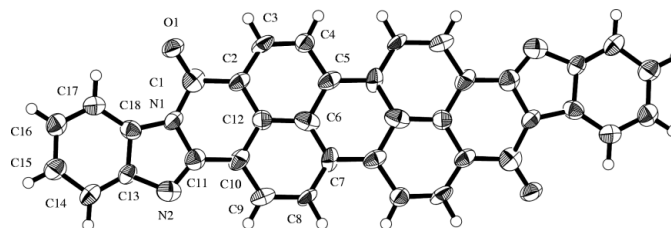
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

N1—C11	1.41 (1)	N2—C13	1.42 (1)
N1—C18	1.39 (1)	C13—C18	1.41 (1)
N2—C11	1.30 (1)		
C4—C5—C7 <sup>i</sup> —C8 <sup>i</sup>	0 (1)		

Symmetry code: (i)  $-x, 1 - y, -z$ .

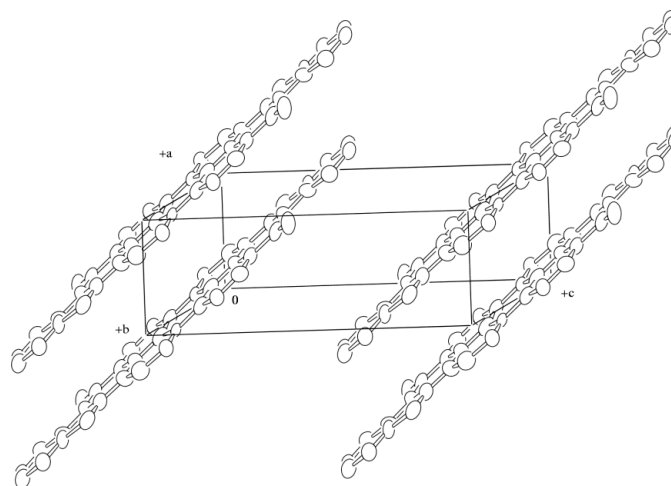
All H atoms were positioned geometrically [ $C\text{--}H = 0.95 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ] and not refined. Since the single crystal needle was slightly curved and the crystallinity was rather poor, the final *R* factor (0.102) remained rather high.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular



**Figure 1**

A view of the molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. Unlabeled atoms are related to labeled atoms by the operation  $(-x, 1 - y, -z)$ .



**Figure 2**

The molecular arrangement of (I) in the crystal structure.

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*.

The author thanks Mr I. Suzuki for experimental assistance.

## References

- Adachi, C., Tokito, S., Tsutsui, T. & Saito, S. (1988). *Jpn J. Appl. Phys.* **27**, L269–273.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Herbst, W. & Hunger, K. (1993). *Industrial Organic Pigments*, pp. 467–475. Weinheim: VCH.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Loutfy, R. O., Hor, A. M., Kazmaier, P. & Tam, M. (1989). *J. Imaging Sci. Technol.* **33**, 151–159.
- Mizuguchi, J. (1981). *Cryst. Res. Technol.* **16**, 695–700.
- Mizuguchi, J. (2003a). *Z. Kristallogr. New Cryst. Struct.* **218**, 137–138.
- Mizuguchi, J. (2003b). *Z. Kristallogr. New Cryst. Struct.* **218**, 139–140.
- Mizuguchi, J. (2005). *Acta Cryst.* **E61**, o1066–o1067.
- Mizuguchi, J. & Shimo, N. (2005). *J. Imaging Sci. Technol.* In the press.
- Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1997). *SHELXS97*. University of Göttingen, Germany.
- Tamizhmani, G., Dopelet, J., Côté, R. & Gravel, D. (1991). *Chem. Mater.* **3**, 1046–1053.