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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)

The title compound, C_{36}H_{16}N_{4}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.

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 photoresistors (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, 2003a,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_{1}; a = 4.729 (2) Å,
b = 8.282 (2) Å, c = 14.693 (4) Å, α = 89.35 (2)°, β = 91.15 (3)°
and γ = 105.83 (3)°] is similar in most lattice parameters to those of
the cis form (II) [P_{2_{1}}/c; a = 4.7501 (6) Å, b = 28.079 (3) Å, c =
8.728 (1) Å and β = 99.21 (1)°], but the former cell volume is
approximately half of the latter. An ORTEPIII plot (Burnett
& Johnson, 1996) of (I) is shown in Fig. 1. The molecule is
totally planar and possesses a center of symmetry. All mol-
ectrons 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

\[ \text{C}_{36}\text{H}_{16}\text{N}_{4}\text{O}_{2} \]

\[ M_r = 536.53 \]

Triclinic, \( \text{P} \)

\[ a = 4.729 (2) \text{ Å} \]

\[ b = 8.282 (2) \text{ Å} \]

\[ c = 14.693 (4) \text{ Å} \]

\[ \alpha = 89.35 (2) \] \( \text{°} \)

\[ \beta = 91.15 (3) \] \( \text{°} \)

\[ \gamma = 104.85 (3) \] \( \text{°} \)

\[ V = 556.2 (3) \text{ Å}^3 \]

\[ Z = 1 \]

\[ \Delta = 1.602 \text{ Mg m}^{-3} \]

\[ \text{Cu} \text{ K} \alpha \text{ radiation} \]

Cell parameters from 3329 reflections

\[ \theta = 3.0-68.2 \] \( \text{°} \)

\[ \mu = 0.82 \text{ mm}^{-1} \]

\[ T = 93.2 \text{ K} \]

\[ \lambda = 0.40 \text{ Å} \]

\[ \text{Needle, black} \]

\[ \text{V} = 0.40 \times 0.05 \times 0.05 \text{ mm} \]

Data collection

Rigaku R-AXIS RAPID Imaging

Plate diffractometer

\( \omega \) scan

Absorption correction: multi-scan

\( \text{ABSCOR: Higashi, 1995} \)

\[ T_{\text{min}} = 0.400, T_{\text{max}} = 0.960 \]

5005 measured reflections

1831 independent reflections

505 reflections with \( F^2 > 2\sigma(F^2) \)

\[ R_{\text{int}} = 0.106 \]

\[ h = -4 \rightarrow 4 \]

\[ k = -9 \rightarrow 9 \]

\[ l = -17 \rightarrow 17 \]

Refinement

Refinement on \( F^2 \)

\[ R(F^2) = 0.102 \]

\[ w = 1/[\sigma(Fo)^2 + 0.042(max(Fo,0) + 2Fo)^2] \]

\( S = 0.93 \)

7404 reflections

190 parameters

H-atom parameters not refined

Table 1

| \( \text{N}1-\text{C}11 \) | 1.41 (1) |
| \( \text{N}1-\text{C}18 \) | 1.39 (1) |
| \( \text{N}2-\text{C}11 \) | 1.30 (1) |
| \( \text{C}4-\text{C}5-\text{C}7-\text{C}8 \) | 0 (1) |

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

All H atoms were positioned geometrically [\( \text{C} - \text{H} = 0.95 \text{ Å} \) 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: \( \text{PROCESS-AUTO} \) (Rigaku, 1998); cell refinement: \( \text{PROCESS-AUTO} \); data reduction: \( \text{TEXSAN} \) (Molecular Structure Corporation, 2001); program(s) used to solve structure: \( \text{SHELXS97} \) (Sheldrick, 1997); program(s) used to refine structure: \( \text{TEXSAN} \); molecular graphics: \( \text{ORTEPIII} \) (Burnett & Johnson, 1996); software used to prepare material for publication: \( \text{TEXSAN} \).

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References


