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N,*N*′-Bis[2-(4-pyridyl)ethyl]perylene-3,4:9,10-bis(dicarboximide) phenol disolvate

Jin Mizuguchi* and Kazuyuki Hino

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

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The title compound, $C_{38}H_{24}N_4O_4\cdot 2C_6H_6O$, is a 1:2 complex of a pyridylethylperylene derivative (EPY) with phenol. The pyridylethylene imide skeleton in a *trans* fashion. The EPY molecule is centrosymmetric. The EPY molecules are stacked along the *a* axis, with a slip angle of about 32°.

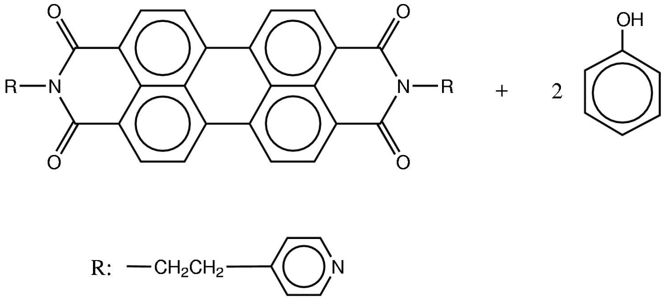
Key indicators

Single-crystal X-ray study
$T = 93$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.039
wR factor = 0.098
Data-to-parameter ratio = 10.6

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

Comment

Perylene compounds are industrially important pigments which cover a variety of shades from red *via* maroon to black (Herbst & Hunger, 1993). The pyridylethylperylene derivative (abbreviated to EPY) in the title compound, (I), has a structure similar to that of the phenylethyl derivative (abbreviated to EPH, also known as pigment black 31). The only difference between EPY and EPH is the pyridyl or phenyl ring. Nevertheless, their colours are strikingly different. EPY (Mizuguchi & Tojo, 2002) is a vivid red, while two crystal modifications of EPH (Hädicke & Graser, 1986; Mizuguchi, 1998) are black. In these two modifications of EPH, the phenylethyl groups are attached to the perylene imide skeleton in a *trans* fashion, while the pyridylethyl groups in EPY are *cis* (Mizuguchi & Tojo, 2002). Because of this, our attention has been focused on the preparation of the *trans* form of EPY, which is expected to be black in colour. This paper reports the structure of the *trans* isomer of EPY, which is black, as its phenol disolvate, (I).



(I)

Fig. 1 shows EPY, which crystallizes with two phenol molecules. The EPY molecule has a centre of symmetry and the two pyridylethyl groups are arranged in a *trans* fashion (C_i symmetry), in contrast with the previous *cis* form of EPY (C_2 symmetry; Mizuguchi & Tojo, 2002). The pyridyl rings are twisted by 31.2 (1)° relative to the perylene–imide skeleton. There is an O—H···N hydrogen bond (Table 2) between the phenol and pyridyl ring of EPY. The phenol ring is twisted by 50.3 (1)° with respect to the pyridyl ring of EPY. The colour of (I) is black, as expected (Mizuguchi & Hino, 2005).

Fig. 2 shows the projection of the structure along the *a* axis. The EPY molecules form columns along the *a* axis, and there are two neighbouring columns composed of phenol molecules.

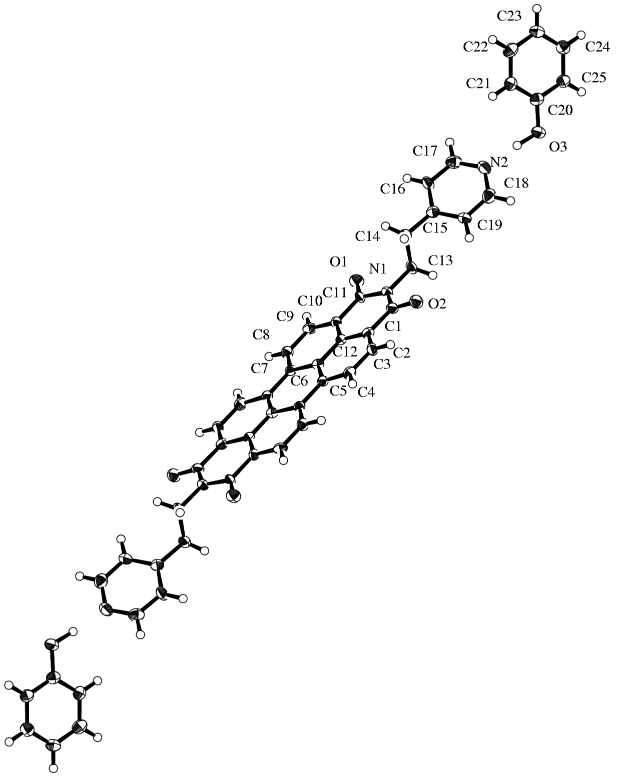


Figure 1
A view of the molecular conformation of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by $(1 - x, 1 - y, 1 - z)$.

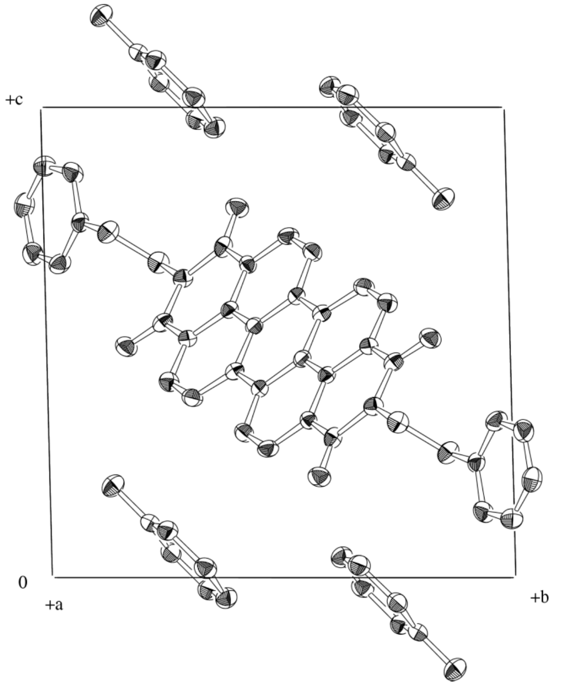


Figure 2
The crystal structure of (I), projected along the *a* axis. H atoms have been omitted.

The polar phenol molecules of each column are arranged so as to cancel their dipole moments, reducing the electrostatic energy. Withinn a column, EPY molecules are stacked with a slip angle of about 32°; this is defined, on the side view of two stacked molecules, as the slipped angle of the upper molecule relative to the lower one along the long molecular axis.

Experimental

EPY was prepared by the reaction of perylenetetracarboxylic dianhydride (10 g) with 4-(aminoethyl)pyridine (8.8 g) at 403 K in water (30 ml) for 5 h. The product was filtered off and the red cake was refluxed for 10 min in *N*,*N*′-dimethylformamide. Black single crystals of (I) (*trans* form) were grown from a 1:1 solution of phenol and ethanol; red crystals (*cis* form) were obtained from solution in nitrobenzene. The use of a protic solvent, such as phenol, was the key to the growth of black crystals of the *trans* form. Since the crystal of (I) was found to include solvent molecules, X-ray intensity data were collected at 93 K. Crystal growth from the vapour phase was also tried but without success, leading to the decomposition of EPY to give a perylene imide derivative known as pigment violet 29.

Crystal data

$C_{38}H_{24}N_4O_4 \cdot 2C_6H_6O$
$M_r = 788.83$
Triclinic, $P\overline{1}$
$a = 6.513$ (2) Å
$b = 12.182$ (2) Å
$c = 12.200$ (2) Å
$\alpha = 89.36$ (1)°
$\beta = 81.11$ (1)°
$\gamma = 76.81$ (2)°
$V = 930.8$ (4) Å^3
$Z = 1$
$D_x = 1.407$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 5227 reflections
$\theta = 3.7$–68.2°
$\mu = 0.76$ mm^{-1}
$T = 93.2$ K
Block, black
0.40 × 0.10 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.797$, $T_{max} = 0.931$
7498 measured reflections
2902 independent reflections
1186 reflections with $F^2 > 2\sigma(F^2)$
$R_{int} = 0.057$
$\theta_{max} = 68.3°$
$h = -5 \rightarrow 6$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.098$
$S = 0.78$
2902 reflections
274 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + \{0.0[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected bond lengths (Å).

O1—C11	1.215 (4)	C5—C6	1.425 (4)
O2—C1	1.223 (4)	C5—C7^{i}	1.476 (5)
N1—C1	1.401 (4)	C6—C7	1.425 (4)
N1—C11	1.408 (4)	C6—C12	1.437 (5)
N1—C13	1.479 (4)	C7—C8	1.379 (4)
C1—C2	1.479 (5)	C8—C9	1.400 (5)
C2—C3	1.373 (4)	C9—C10	1.365 (5)
C2—C12	1.407 (4)	C10—C11	1.491 (5)
C3—C4	1.399 (5)	C10—C12	1.408 (4)
C4—C5	1.389 (5)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H18···N2	1.08 (4)	1.65 (4)	2.717 (4)	170 (3)

The hydroxy H atom (H18) of phenol was found in a difference Fourier map and its coordinates were refined, with $U_{\rm iso}$(H) = $1.3U_{\rm eq}$(O). All other H atoms were positioned geometrically and included in the riding-model approximation, with C—H distances of 0.95 Å, and with $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C).

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

References

Burnett, M. N. & Johnson, C. K.(1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory. Tennessee, USA.

Hädicke, E. & Graser, F. (1986). *Acta Cryst.* C**42**, 189–195.

Herbst, W. & Hunger, K. (1993). *Industrial Organic Pigments*, pp. 467–475. Weinheim: VCH.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Mizuguchi, J. (1998). *Acta Cryst.* C**54**, 1479–1481.

Mizuguchi, J. & Hino, K. (2005). *Dyes Pigments.* Submitted.

Mizuguchi, J. & Tojo, K. (2002). *Z. Kristallogr. New Cryst. Struct.* **217**, 247–248.

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.