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

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The title compound, $C_{38}H_{24}N_4O_4\cdot 2C_7H_8O$, is a 1:2 complex of a pyridylethylperylene derivative, EPY, with *m*-cresol. The EPY molecule has a centre of symmetry and the pyridylethyl groups are attached to the perylene–imide skeleton in a *trans* fashion. The EPY molecules are stacked along the *a* axis with a slip angle of about 47°.

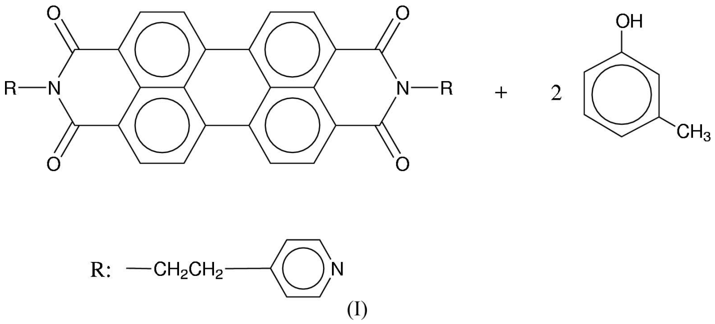
Key indicators

Single-crystal X-ray study
$T = 93$ K
Mean σ(C–C) = 0.008 Å
R factor = 0.100
wR factor = 0.118
Data-to-parameter ratio = 12.0

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, covering a variety of shades from red *via* maroon to black (Herbst & Hunger, 1993). *N*,*N*′-Bis[2-(4-pyridyl)ethyl]-perylene-3,4:9,10-bis(dicarboximide) is a pyridylethyl derivative, here abbreviated to EPY. It has a similar structure to that of the phenylethyl derivative, here abbreviated to EPH and also known as pigment black 31. The only difference between EPY and EPH is the pyridyl or phenyl ring. Nevertheless, the colours are strikingly different. EPY (Mizuguchi & Tojo, 2002) is 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 show a black colour. We have recently isolated a black crystal of the *trans* form from a 1:1 mixed solvent of phenol and ethanol, EPY·2(phenol) (Mizuguchi & Hino, 2005*a*). The present paper deals with another complex of the *trans* form, EPY·2(*m*-cresol), (I), recrystallized from *m*-cresol and which is red–black.



(I)

Fig. 1 shows the structure of (I), in which one molecule of EPY crystallizes with two *m*-cresol molecules. The EPY molecule has a centre of symmetry and the two pyridylethyl groups are arranged in a *trans* fashion (C_i symmetry), in marked contrast to the previous *cis* form (C_2 symmetry; Mizuguchi & Tojo, 2002). The pyridyl rings deviate from the perylene imide skeleton by 5.2 (2)°.

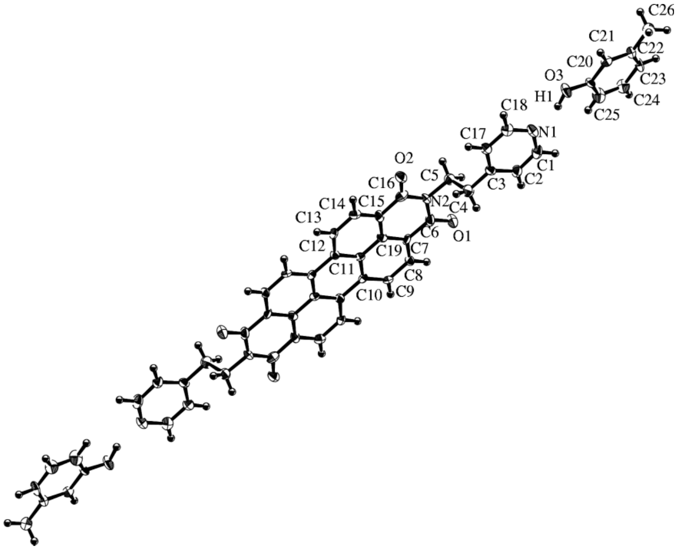


Figure 1
A view of the molecular conformation of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related to labelled atoms by $1 - x, 1 - y, 2 - z$.

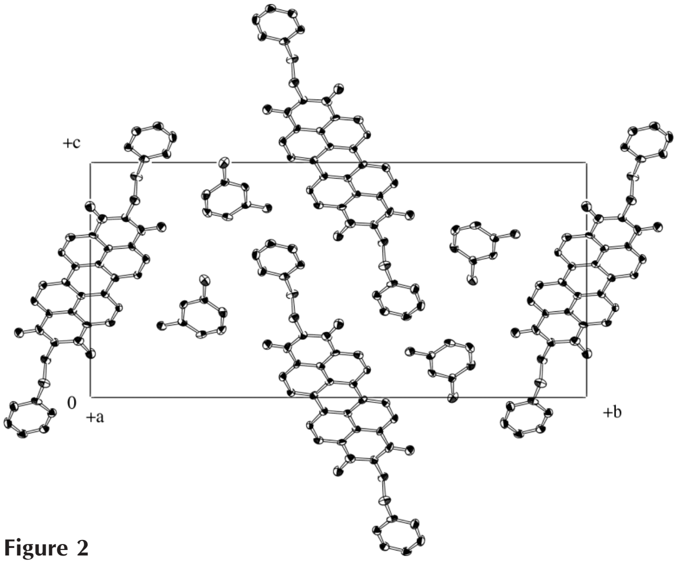


Figure 2
Projection of the crystal structure of (I) along the *a* axis. H atoms have been omitted.

There is an intermolecular O—H···N hydrogen bond (Table 2) between the *m*-cresol molecule and the pyridyl group of EPY. The *m*-cresol molecule is twisted by 18.6 (2)° with respect to the pyridyl ring. The colour of complex (I) is reddish-black, as expected (Mizuguchi & Hino, 2005*b*).

Fig. 2 shows the projection of the crystal structure along the *a* axis. The EPY molecules form columns along the *a* axis, while there are two neighbouring columns composed of *m*-cresol molecules. The polar *m*-cresol molecules of each column are arranged so as to cancel their dipole moments to reduce the electrostatic energy. Within a column, the EPY molecules are stacked with a slip angle of about 47°, which is defined, in a 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 perylene tetracarboxylic dianhydride (10 g) with aminoethylpyridine (8.8 g) at 403 K in water (30 ml) for 5 h. The product was filtered and the red cake was then refluxed for 10 min in *N*,*N*′-dimethylformamide. Single crystals of a reddish-black colour (*trans* form) were grown from solution in *m*-cresol, whereas red crystals (*cis* form) were obtained from solution in nitrobenzene. The use of a protic solvent such as *m*-cresol was the key to the growth of black crystals of the *trans* form. Since the reddish-black crystal of (I) was found to include solvent molecules, X-ray intensity data were collected at 93 K. Obtaining single crystals from the vapour phase was also attempted but without success, leading to the decomposition of EPY to give a perylene imide derivative known as pigment violet 29.

Crystal data

$C_{38}H_{24}N_4O_4 \cdot 2C_7H_8O$
$M_r = 816.88$
Monoclinic, $P2_1/c$
$a = 4.903$ (6) Å
$b = 29.26$ (4) Å
$c = 13.96$ (2) Å
$\beta = 97.65$ (6)°
$V = 1985$ (4) Å^3
$Z = 2$

$D_x = 1.367$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 4038 reflections
$\theta = 3.0$–65.6°
$\mu = 0.73$ mm^{-1}
$T = 93.2$ K
Needle, red
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)
$T_{\min} = 0.618$, $T_{\max} = 0.930$
3443 measured reflections

3363 independent reflections
1335 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.147$
$\theta_{\max} = 68.2°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 35$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.100$
$wR(F^2) = 0.118$
$S = 1.00$
3363 reflections
280 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + \{0.025[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}
Extinction correction: none

Table 1
Selected bond lengths (Å).

O1—C6	1.223 (7)	C10—C11	1.437 (7)
O2—C16	1.233 (7)	C10—C12$^{\rm i}$	1.485 (7)
N2—C5	1.493 (7)	C11—C12	1.429 (8)
N2—C6	1.405 (7)	C11—C19	1.425 (7)
N2—C16	1.412 (7)	C12—C13	1.402 (7)
C6—C7	1.469 (8)	C13—C14	1.393 (7)
C7—C8	1.370 (7)	C14—C15	1.387 (8)
C7—C19	1.406 (8)	C15—C16	1.465 (8)
C8—C9	1.410 (7)	C15—C19	1.399 (8)
C9—C10	1.384 (7)	C17—C18	1.387 (7)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···N1$^{\rm ii}$	1.00	1.80	2.761 (5)	161

The H atom attached to the O atom was found in a difference-density map and its positional parameters were fixed with $U_{\rm iso}(H) = 1.1U_{\rm eq}(O)$. All other H atoms were positioned geometrically and included in a riding-model approximation, with C—H = 0.95 Å and with $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$. The maximum residual density is located 1.25 Å from atom C5.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SYSTEM90* (Hou *et al.*, 1994); 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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