

3,3'-(1,4-Dioxopyrrolo[3,4-c]pyrrole-3,6-diyl)-
dibenzonitrile dimethylacetamide disolvate

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The title compound, $C_{20}H_{10}N_4O_2 \cdot 2C_4H_9NO$, is a solvated centrosymmetric pigment molecule (*m*-CN DPP) with the two dimethylacetamide (DMA) molecules connected *via* N—H···O hydrogen bonds. One *m*-CN DPP molecule is surrounded by six DMA molecules in the crystal structure.

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Key indicators

Single-crystal X-ray study
 $T = 296$ K
 Mean $\sigma(C-C) = 0.010$ Å
 R factor = 0.109
 wR factor = 0.347
 Data-to-parameter ratio = 20.8

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

Comment

Diketopyrrolopyrroles (DPPs) are industrially important red pigments which belong to the class of hydrogen-bonded pigments (Herbst & Hunger, 1993). In these pigments, there are two-dimensional N—H···O intermolecular hydrogen bonds between the N—H group of one molecule and the O atom of a neighbouring one (Mizuguchi, Grubenmann *et al.*, 1992; Mizuguchi *et al.*, 1993; Mizuguchi & Matsumoto, 2000). Among these, *m*-CN DPP and *m*-Cl DPP are characterized by a yellowish-red colour rather than vivid red. To elucidate the mechanism for this, single crystals of *m*-CN DPP have previously been grown from the vapour phase. The structure analysis (Mizuguchi & Matsumoto, 2000) revealed that the significant π - π overlap along the stacking axis is primarily responsible for the yellowish colour (Mizuguchi & Rihs, 1992). In the present investigation, a further attempt was made to grow solvated crystals of *m*-CN DPP in order to study the influence of intermolecular interactions on the optical absorption, because the solvent molecules act as the spacers between *m*-CN DPP molecules to block their direct intermolecular interaction.

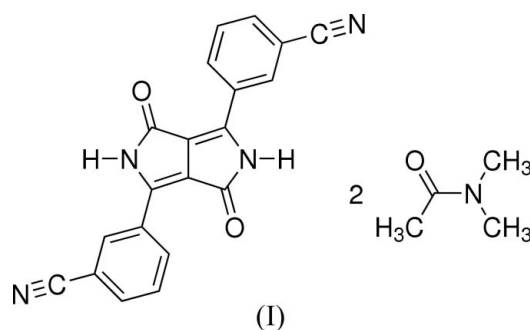


Fig. 1 shows an *ORTEP* (Burnett & Johnson, 1996) plot of the title compound, (I). Two DMA molecules are connected to the *m*-CN DPP molecule through N—H···O hydrogen bonds (Table 2). The *m*-CN DPP molecule is centrosymmetric but not entirely planar, because the benzene rings are twisted in the same direction out of the plane of the heterocyclic ring system by $4.1(3)^\circ$. The N2—C10—C3 angle is $177.8(11)^\circ$ and the C10—C3 distance is $1.448(14)$ Å. The corresponding

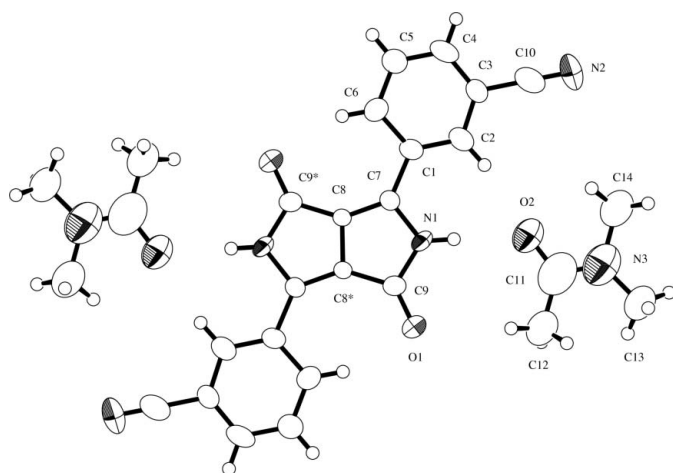


Figure 1

A view of the molecular structure of (I), showing 50% probability displacement ellipsoids. Atoms C8*/C9* and unlabelled atoms are related to C8/C9 and other labelled atoms by the symmetry operation $(1 - x, -y, 1 - z)$.

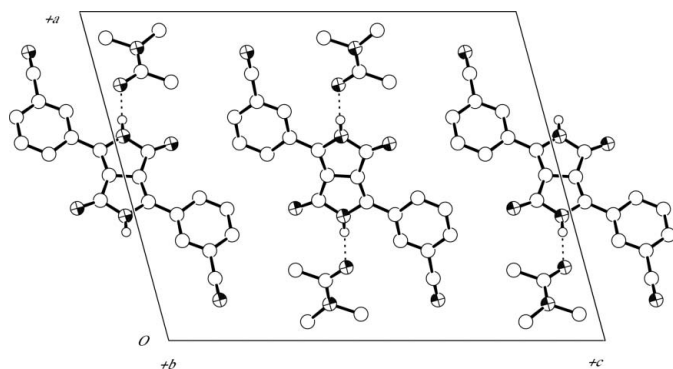


Figure 2

A projection of the crystal structure of (I) down the b axis. H atoms have been omitted except for those involved in hydrogen bonds (dotted lines).

values in solvent-free m -CN DPP (Mizuguchi & Matsumoto, 2000) are $10.1(3)^\circ$, $179.6(3)^\circ$ and $1.434(4) \text{ \AA}$, respectively.

Fig. 2 shows a projection of the crystal structure down the b axis. The m -CN DPP and DMA molecules are stacked with an interplanar spacing of $4.020(5) \text{ \AA}$ ($= b$). One m -CN DPP molecule is surrounded by six DMA molecules in the crystal structure. Therefore, the absorption spectrum of (I) in the solid state is found to be quite similar to that in a DMA solution. In addition, the extent of π - π overlap is found to be insignificant compared with that of the solvent-free crystals of m -CN DPP (Mizuguchi & Matsumoto, 2000).

Experimental

m -CN DPP was obtained from CIBA Specialty Chemicals and purified three times by sublimation under vacuum, using a two-zone furnace (Mizuguchi, 1981). Single crystals of (I) were grown by gradual cooling from a DMA solution prepared at about 420 K. After a week, a number of light-orange crystals were obtained in the form of platelets.

Crystal data

$\text{C}_{20}\text{H}_{10}\text{N}_4\text{O}_2 \cdot 2\text{C}_4\text{H}_9\text{NO}$
 $M_r = 512.56$
 Monoclinic, $P2_1/c$
 $a = 16.129(5) \text{ \AA}$
 $b = 4.020(5) \text{ \AA}$
 $c = 20.676(6) \text{ \AA}$
 $\beta = 105.18(2)^\circ$
 $V = 1293.8(17) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.316 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 0.09 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Platelet, orange
 $0.40 \times 0.10 \times 0.03 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.968$, $T_{\max} = 0.997$
 3078 measured reflections
 2975 independent reflections

665 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.082$
 $\theta_{\max} = 27.5^\circ$
 3 standard reflections
 every 100 reflections
 intensity decay: 22.0%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.109$
 $wR(F^2) = 0.347$
 $S = 1.14$
 2975 reflections
 143 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.85 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.37 \text{ e \AA}^{-3}$

Table 1

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

O1—C9	1.230 (8)	C7—C8	1.365 (10)
N1—C7	1.400 (8)	C8—C8 ⁱ	1.417 (9)
N1—C9	1.410 (10)	C8—C9 ⁱ	1.452 (9)
C7—N1—C9	110.3 (5)	C7—C8—C9 ⁱ	143.3 (6)
N1—C7—C8	108.6 (6)	O1—C9—N1	123.0 (6)
C7—C8—C8 ⁱ	108.5 (5)	N1—C9—C8 ⁱ	104.4 (5)

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1N \cdots O2	0.86	2.03	2.884 (8)	172

Since the reflection data of the solvated crystal were collected at room temperature, the solvent DMA molecules were rather mobile, as shown by the significant decay of the reflection intensity during the measurement, as well as by the high atomic displacement parameters of DMA. For this reason, the bond distances and angles of DMA were restrained [$\text{C11—C12} = 1.540(1) \text{ \AA}$, $\text{C11—O2} = 1.540(1) \text{ \AA}$, $\text{C11—N3} = 1.350(1) \text{ \AA}$, $\text{N3—C13} = 1.460(1) \text{ \AA}$ and $\text{N3—C14} = 1.460(1) \text{ \AA}$, and $\text{C11—N3—C13} = 120.20(4)^\circ$ and $\text{C13—N3—C14} = 120.20(4)^\circ$]. The methyl H atoms were constrained to an ideal geometry, with $\text{C—H} = 0.96 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl groups C13 and C14 were allowed to rotate freely about their C—C bond, but the orientation of methyl group C12 was calculated in order to avoid an abnormally short $\text{H} \cdots \text{H}$ distance. All other H atoms were positioned geometrically and constrained to ride on their parent atoms, with $\text{C—H} = 0.93 \text{ \AA}$ and $\text{N—H} = 0.86 \text{ \AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: *MSC/AFC Diffractometer Control Software* (Rigaku/MSC, 2000); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR2002* (Burla *et al.*,

2003); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

References

- Burla, M. C., Camalli, M., Carrozzini, B., Cascarano, G. L., Giacovazzo, C., Polidori, G. & Spagna, R. (2003). *J. Appl. Cryst.* **36**, 1103.
- 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. 447–464. Weinheim: VCH.
- Mizuguchi, J. (1981). *Kristallogr. Tech.* **16**, 695–700.
- Mizuguchi, J., Grubenmann, A. & Rihs, G. (1993). *Acta Cryst.* **B49**, 1056–1060.
- Mizuguchi, J., Grubenmann, A., Wooden, G. & Rihs, G. (1992). *Acta Cryst.* **B48**, 696–700.
- Mizuguchi, J. & Matsumoto, S. (2000). *Z. Kristallogr. New Cryst. Struct.* **215**, 195–196.
- Mizuguchi, J. & Rihs, G. (1992). *Ber. Bunsen-Ges. Phys. Chem.* **96**, 597–606.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Rigaku/MSK (2000). *MSK/AFK Diffractometer Control Software*. Rigaku/MSK, The Woodlands, Texas, USA.
- Rigaku/MSK (2005). *CrystalStructure*. Version 3.7.0. Rigaku/MSK, The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.