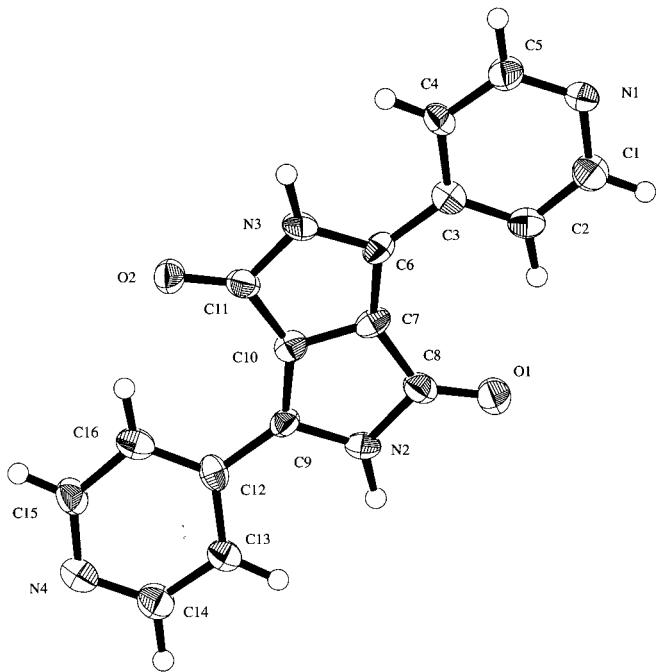


## Appendix II

### Crystal structure of 3,6-bis(4'-pyridyl)-pyrrolo[3,4-c]pyrrole-1,4-dione, C<sub>16</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>, at 93 K

#### *para*-DPPP: phase II



two-zone furnace [2]. The single crystals were grown from the vapor phase in a closed system. After 48 h, a number of red needle crystals as well as platelet crystals were obtained. However, the single crystals obtained were quite small. This resulted in a rather low number of observed reflections ( $N(hkl)_{gt}$ ) for the crystal under study.

#### Discussion

Diketopyrrolopyrrole (abbreviated to DPP) pigments are industrially important red pigments based on the novel diketopyrrolopyrrole chromophore [3]. DPPs are also used as colorants for imaging areas as well as red color filters for LCD applications. We have carried out a series of investigations on the crystal structures [4-10] as well as the electronic properties of DPP pigments [11-14]. Previously, we have clarified that the structure of the title compound (3,6-bis(4'-pyridyl)-pyrrolo-[3,4-c]-pyrrole-1,4-dione) is isomorphous with that of 3,6-diphenylpyrrolo[3,4-c]pyrrole-1,4-dione (triclinic form) [13] where the

#### Abstract

C<sub>16</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>, monoclinic,  $P12_1/n$  (No.14),  $a = 3.6951(7)$  Å,  $b = 18.201(2)$  Å,  $c = 18.456(2)$  Å,  $\beta = 94.68(1)^\circ$ ,  $V = 1237.1$  Å<sup>3</sup>,  $Z = 4$ ,  $R_{gt}(F) = 0.068$ ,  $wR_{ref}(F^2) = 0.129$ ,  $T = 93$  K.

#### Source of material

The title compound was synthesized from benzonitrile and dimethyl succinate by the method previously described [1]. The product was purified by sublimation at about 625 K, using a

difference in chemical formula is only pyridyl or phenyl ring. In the present paper, we report a new crystal phase (monoclinic form). The molecular symmetry is  $C_1$  as shown in the picture. The two pyridyl rings on each side of the heterocyclic ring system are twisted asymmetrically in the same direction:  $4.2(2)^\circ$  at the C3—C6 bond and  $15.3(2)^\circ$  at the C9—C12 bond. The heterocyclic ring system is almost planar as characterized by a dihedral angle of  $179.7(2)^\circ$ . There are two kinds of intermolecular hydrogen bonds: one is between the N—H group of one molecule and the O atom of the neighboring one (N—H $\cdots$ O: 2.84 Å) and the other is between the N—H group and the N atom of the pyridyl ring (N—H $\cdots$ N: 2.89 Å). That is, one central molecule is hydrogen bonded to the neighboring one along the short-molecular axis through two N—H $\cdots$ O bonds. At the same time, the central molecule is also bonded to two other neighboring molecules along the long-molecular axis through a single N—H $\cdots$ N bond for each molecule. Because of these intermolecular hydrogen bonds, all molecules are pairwise arranged on the entire molecular plane. The present hydrogen-bond network is quite unique and is totally different from the one found for all other DPP pigments [4-10]. In these DPP derivatives, one molecule is hydrogen-bonded to two neighboring molecules along the short-molecular axis through four N—H $\cdots$ O bonds, forming chains of intermolecular hydrogen bonds.

**Table 1. Data collection and handling.**

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Crystal:	red block, size $0.03 \times 0.05 \times 0.15$ mm
Wavelength:	Cu $K\alpha$ radiation (1.5419 Å)
$\mu$ :	$8.89 \text{ cm}^{-1}$
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 60 frames, $\Delta\omega = 15^\circ$
$2\theta_{\max}$ :	$135.9^\circ$
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$ :	13098, 2114
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$ , 853
$N(\text{param})_{\text{refined}}$ :	199
Programs:	SHELXS-86 [15], teXsan [16], ORTEPII [17]

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**Table 2. Atomic coordinates and displacement parameters (in Å<sup>2</sup>).**

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(1)	4e	-0.0191	0.0103	0.1489	0.0434
H(2)	4e	0.2467	-0.0781	0.2255	0.0307
H(3)	4e	0.4994	0.0829	0.3751	0.0303
H(4)	4e	0.2160	0.1656	0.2949	0.0383
H(5)	4e	0.5935	-0.3123	0.3311	0.0352
H(6)	4e	0.7696	0.0070	0.4435	0.0376
H(7)	4e	0.9561	-0.3825	0.3917	0.0309
H(8)	4e	1.2397	-0.4660	0.4735	0.0385
H(9)	4e	1.2888	-0.3194	0.6314	0.0403
H(10)	4e	1.0406	-0.2294	0.5560	0.0425

**Table 3. Atomic coordinates and displacement parameters (in Å<sup>2</sup>).**

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
O(1)	4e	0.312(1)	-0.2054(2)	0.2482(2)	0.048(3)	0.034(2)	0.037(2)	0.001(2)	-0.005(2)	0.001(2)
O(2)	4e	1.0534(9)	-0.0996(2)	0.5252(2)	0.042(3)	0.030(2)	0.027(2)	-0.001(2)	-0.001(2)	0.001(2)
N(1)	4e	0.075(1)	0.0972(2)	0.2144(2)	0.031(3)	0.024(2)	0.035(3)	0.003(2)	0.003(2)	0.000(2)
N(2)	4e	0.616(1)	-0.2612(2)	0.3484(2)	0.041(4)	0.018(2)	0.038(3)	0.003(2)	0.002(2)	-0.002(2)
N(3)	4e	0.745(1)	-0.0436(2)	0.4260(2)	0.048(4)	0.014(2)	0.039(3)	0.001(2)	-0.002(3)	0.001(2)
N(4)	4e	1.296(1)	-0.4014(2)	0.5605(2)	0.038(3)	0.033(3)	0.045(3)	0.005(2)	0.002(3)	0.005(2)
C(1)	4e	0.087(1)	0.0251(3)	0.1966(3)	0.043(4)	0.034(3)	0.038(4)	-0.003(3)	0.005(3)	0.004(3)
C(2)	4e	0.243(1)	-0.0279(3)	0.2420(3)	0.030(4)	0.030(3)	0.039(3)	0.002(3)	0.008(3)	-0.002(3)
C(3)	4e	0.398(1)	-0.0082(3)	0.3092(3)	0.025(4)	0.027(3)	0.035(3)	-0.005(3)	0.005(3)	0.004(3)
C(4)	4e	0.387(1)	0.0662(3)	0.3283(3)	0.033(4)	0.028(3)	0.031(3)	0.004(3)	0.002(3)	0.007(3)
C(5)	4e	0.226(2)	0.1145(3)	0.2799(3)	0.039(4)	0.029(3)	0.036(3)	-0.004(3)	0.001(3)	-0.003(3)
C(6)	4e	0.565(1)	-0.0622(3)	0.3597(3)	0.034(4)	0.028(3)	0.027(3)	-0.005(3)	0.001(3)	-0.007(3)
C(7)	4e	0.577(1)	-0.1381(3)	0.3560(3)	0.031(4)	0.024(3)	0.033(3)	-0.008(3)	0.004(3)	-0.009(3)
C(8)	4e	0.482(2)	-0.2004(3)	0.3086(3)	0.035(4)	0.028(3)	0.033(3)	0.006(3)	0.006(3)	0.006(3)
C(9)	4e	0.788(1)	-0.2422(3)	0.4147(3)	0.025(4)	0.026(3)	0.025(3)	-0.001(3)	0.000(3)	-0.007(3)
C(10)	4e	0.767(1)	-0.1657(3)	0.4193(3)	0.026(4)	0.029(3)	0.031(3)	-0.003(3)	0.003(3)	-0.003(3)
C(11)	4e	0.882(2)	-0.1039(3)	0.4651(3)	0.035(4)	0.028(3)	0.032(3)	0.008(3)	0.007(3)	0.002(3)
C(12)	4e	0.957(1)	-0.2955(3)	0.4657(3)	0.022(4)	0.034(3)	0.030(3)	-0.003(3)	-0.002(3)	0.007(3)
C(13)	4e	1.026(1)	-0.3671(3)	0.4416(3)	0.033(4)	0.027(3)	0.035(3)	0.002(3)	0.003(3)	0.003(2)
C(14)	4e	1.194(2)	-0.4150(3)	0.4909(3)	0.044(4)	0.032(3)	0.040(3)	0.000(3)	0.003(3)	0.005(3)
C(15)	4e	1.230(1)	-0.3321(3)	0.5810(3)	0.046(4)	0.032(3)	0.032(3)	0.000(3)	-0.001(3)	0.009(3)
C(16)	4e	1.069(1)	-0.2780(3)	0.5369(3)	0.037(4)	0.025(3)	0.044(3)	0.001(3)	0.005(3)	0.003(3)

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