Crystal structure of 3,6-diphenylpyrrolo[3,4-*c*]pyrrole-1,4-dione—3,6-bis(4-*tert*-butylphenyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (1:1), $(C_{18}H_{12}N_2O_2) \cdot (C_{26}H_{28}N_2O_2)$

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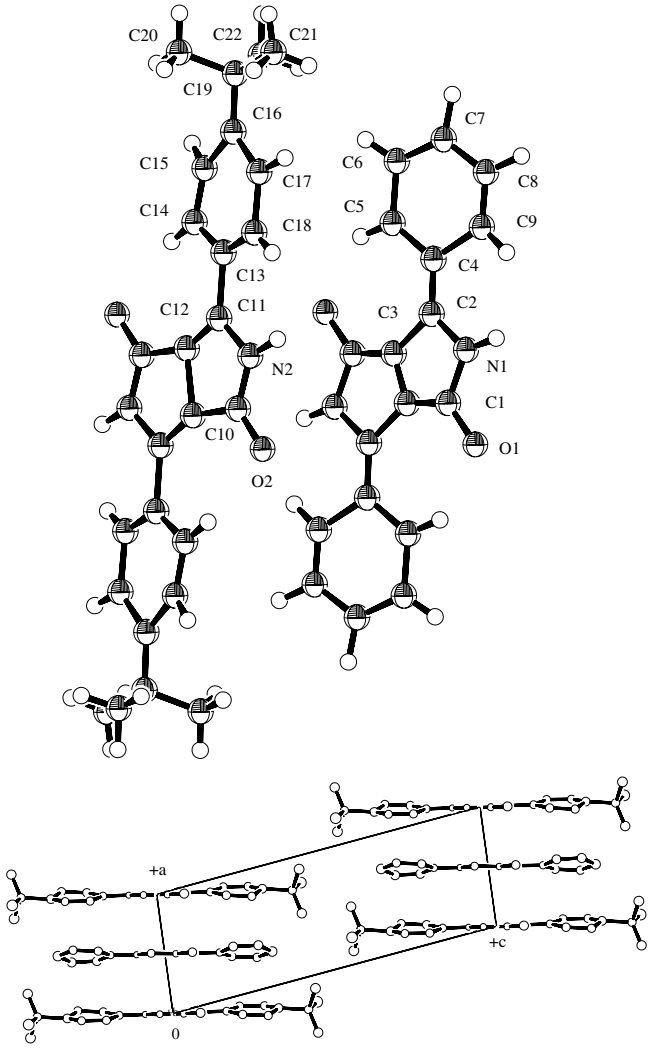

Abstract

$C_{44}H_{40}N_4O_4$, triclinic, $P\bar{1}$ (No. 2), $a = 6.565(1)$ Å, $b = 7.253(2)$ Å, $c = 18.355(4)$ Å, $\alpha = 83.48(2)°$, $\beta = 82.43(2)°$, $\gamma = 87.03(2)°$, $V = 860.2$ Å^3, $Z = 1$, $R_{gt}(F) = 0.138$, $wR_{obs}(F) = 0.160$, $T = 93$ K.

Source of material

Diketo-diphenylpyrrolopyrrole (DPP) and diketo-bis(*tert*-butylphenyl)pyrrolo pyrrole (BTB-DPP) were obtained from Ciba Specialty Chemicals. The 1:1 mixed crystal (MX-DPP) was prepared by deprotonation of DPP and BTB-DPP with sodium hydroxide, followed by protonation with hydrochloric acid [1]. MX-DPP was then purified by sublimation at about 610 K, using two-zone furnace [2]. Organic pigments are quite insoluble in organic solvents. Thus, after a long optimization of the growth parameters, it is possible to grow single crystals from the vapor phase in a closed system. Red platelet crystals of the title compound were obtained after 48 hours.

Experimental details

The present crystal is extremely small and the crystallinity is rather poor. Therefore, only isotropic refinement has been carried out on MX-DPP. Nevertheless, the bond parameters seem to be quite reasonable. Refinement was done using 769 reflections with $I_{obs} > 1\,\sigma(I_{obs})$. However, the threshold expression of $I_{obs} > 2\,\sigma(I_{obs})$ was used for calculating $R_{gt}(F)$ (409 reflections). No additional peaks were found on difference Fourier maps.

Discussion

The 1:1 mixed crystal (MX-DPP) contains two kinds of diketopyrrolopyrroles known as industrially important red pigments: diketo-diphenylpyrrolopyrrole (DPP) [3,4] and diketo-bis(*tert*-butylphenyl)pyrrolopyrrole (BTB-DPP) [5]. We have recently found that MX-DPP composed of DPP and BTB-DPP gives practically the same electronic spectra as well as the X-ray diffraction diagrams as those of the hybrid compound of DPP and BTB-DPP; diketo-mono(*tert*-butylphenyl) pyrrolopyrrole (MTB-DPP) [1,6]. The present coincidence of these physical properties is of great scientific interest and also of industrial interest, because the color specified by expensive MTB-DPP (due to the synthesis of asymmetrical molecules) can be achieved by inexpensive DPP and BTB-DPP (due to the synthesis of symmetrical molecules). Previously, we have reported the crystal structure of MTB-DPP [7]. This shows that there is a NH···O hydrogen bond network and the molecules are arranged in a fashion "bricks in a brick wall". In addition, the *t*-butyl group of MTB-DPP faces the phenyl ring of the neighboring one.

The structure of the present MX-DPP is found to be isomorphous with that of MTB-DPP. The two component molecules are shown in top figure. Each molecule has a symmetry of C_i. The two phenyl rings on each side of the heterocyclic ring system are twisted symmetrically in the same direction: 13° in DPP and 11° in BTB-DPP with respect to the heterocyclic system. The both molecules are stacked alternately in a fashion "bricks in a brick wall" just as found in MTB-DPP [7]. On each molecular plane of DPP and BTB-DPP, there are chains of intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one. This forms a two-dimensional hydrogen

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bond network as found in all pyrrolopyrrole pigments [4,5, 7-10] and causes the very good thermal and solvent resistance of the hydrogen bonded DPP pigments. In addition, the *t*-butyl group of one BTB-DPP molecule faces the phenyl ring of the neighboring DPP molecule in the lattice plane (bottom figure) as observed exactly in MTB-DPP. The present local similarity as characterized by "*t*-butyl group & phenyl ring" (in other words, the same molecular environment) prevail throughout the crystal in both MX-DPP and MTB-DPP. This explains the coincidence of the reflection spectra as well as of the X-ray diffraction diagrams in MX-DPP and MTB-DPP.

Table 1. Data collection and handling.

Crystal:	red platelet, size 0.02 × 0.05 × 0.30 mm
Wavelength:	Cu K_α radiation (1.5419 Å)
μ:	6.86 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 44 frames, $\Delta\omega = 5°$
$2\theta_{max}$:	130°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8001, 891
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 1\ \sigma(I_{obs})$, 769
$N(param)_{refined}$:	105
Programs:	SHELXS-86 [11], teXsan [12], ORTEPII [13], ABSCOR [14]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
O(1)	2*i*	–0.545(3)	–0.674(3)	0.082(1)	0.042(6)
O(2)	2*i*	–1.059(3)	–1.172(3)	0.083(1)	0.051(7)
N(1)	2*i*	–0.462(4)	–0.710(4)	–0.041(2)	0.059(9)
N(2)	2*i*	–0.976(3)	–1.223(3)	–0.038(1)	0.012(5)
C(1)	2*i*	–0.526(4)	–0.780(4)	0.029(2)	0.018(7)
C(2)	2*i*	–0.442(5)	–0.854(5)	–0.086(2)	0.05(1)
C(3)	2*i*	–0.479(4)	–1.028(4)	–0.032(1)	0.024(7)
C(4)	2*i*	–0.398(4)	–0.838(4)	–0.158(2)	0.035(8)
C(5)	2*i*	–0.412(5)	–0.980(4)	–0.204(2)	0.051(9)
C(6)	2*i*	–0.354(5)	–0.960(4)	–0.285(2)	0.055(9)
C(7)	2*i*	–0.294(4)	–0.782(3)	–0.315(1)	0.021(6)
C(8)	2*i*	–0.276(4)	–0.635(4)	–0.273(1)	0.039(8)
C(9)	2*i*	–0.315(4)	–0.666(3)	–0.201(1)	0.031(7)
C(10)	2*i*	–1.024(5)	–1.282(4)	0.032(2)	0.037(8)
C(11)	2*i*	–0.945(4)	–1.361(3)	–0.085(1)	0.017(7)
C(12)	2*i*	–0.960(4)	–1.522(4)	–0.043(1)	0.025(7)
C(13)	2*i*	–0.886(4)	–1.338(4)	–0.171(2)	0.027(7)
C(14)	2*i*	–0.838(4)	–1.488(3)	–0.208(1)	0.022(6)
C(15)	2*i*	–0.788(5)	–1.441(4)	–0.279(2)	0.06(1)
C(16)	2*i*	–0.794(6)	–1.272(6)	–0.330(3)	0.10(1)
C(17)	2*i*	–0.853(5)	–1.134(4)	–0.280(2)	0.050(9)
C(18)	2*i*	–0.919(4)	–1.149(3)	–0.201(1)	0.022(6)
C(19)	2*i*	–0.745(4)	–1.258(3)	–0.406(1)	0.032(7)
C(20)	2*i*	–0.885(5)	–1.365(4)	–0.436(2)	0.062(9)
C(21)	2*i*	–0.764(4)	–1.046(4)	–0.438(2)	0.051(8)
C(22)	2*i*	–0.529(5)	–1.325(4)	–0.424(2)	0.062(9)
H(1)	2*i*	–0.4384	–0.5840	–0.0576	0.067
H(2)	2*i*	–0.4546	–1.0976	–0.1853	0.063
H(3)	2*i*	–0.3960	–1.0448	–0.3130	0.064
H(4)	2*i*	–0.2356	–0.7579	–0.3731	0.066
H(5)	2*i*	–0.2197	–0.5115	–0.2948	0.049
H(6)	2*i*	–0.3302	–0.5619	–0.1690	0.058
H(7)	2*i*	–0.9672	–1.0930	–0.0614	0.043
H(8)	2*i*	–0.8439	–1.6039	–0.1808	0.043
H(9)	2*i*	–0.7065	–1.5519	–0.3083	0.043
H(10)	2*i*	–0.8568	–1.0012	–0.3003	0.054
H(11)	2*i*	–0.9568	–1.0505	–0.1765	0.058
H(12)	2*i*	–0.5133	–1.4515	–0.4063	0.062
H(13)	2*i*	–0.4963	–1.3143	–0.4780	0.062
H(14)	2*i*	–0.4325	–1.2544	–0.4060	0.062
H(15)	2*i*	–0.9105	–1.0154	–0.4175	0.113
H(16)	2*i*	–0.7568	–1.0410	–0.4877	0.113
H(17)	2*i*	–0.6800	–0.9759	–0.4188	0.113
H(18)	2*i*	–0.8704	–1.4910	–0.4189	0.061
H(19)	2*i*	–0.8687	–1.3441	–0.4874	0.061
H(20)	2*i*	–1.0221	–1.3199	–0.4169	0.061

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