Crystal structure of 3-[4-(1,1-dimethylethyl)phenyl]-2,5-dihydro-6-phenylpyrrolo[3,4-*c*]pyrrole-1,4-dione, $C_{22}H_{20}N_2O_2$, *at 93 K*

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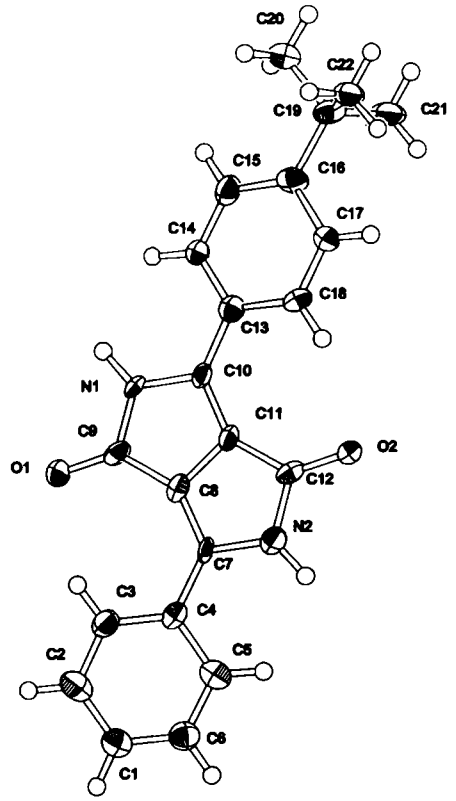

Abstract

$C_{22}H_{20}N_2O_2$, triclinic, $P\bar{1}$ (No. 2), $a = 6.450(2)$ Å, $b = 7.089(4)$ Å, $c = 17.951(6)$ Å, $\alpha = 84.85(4)°$, $\beta = 86.10(1)°$, $\gamma = 87.41(4)°$, $V = 815.0$ Å^3, $Z = 2$, $R_{gt}(F) = 0.114$, $wR_{ref}(F^2) = 0.210$, $T = 93$ K.

Source of material

The title compound was synthesized by the method previously described [1]. The sample was purified by sublimation at about 610 K, using a two-zone furnace [2]. However, the single crystals were quite small and their crystallinity was poor as reflected in the rather high R values. The single crystals were grown from the vapor phase in a closed system. After 48 hours, a number of red platelet crystals were obtained.

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. Up to now, five DPP-derivatives are on the market and most of their structures have already been analyzed [3-7]. The title compound (MTB-DPP) is an asymmetrical molecule characterized by an extremely large bathochromic shift on going from solution to the solid state as compared with that of other DPP analogues. As shown in the figure, the molecule is characterized by the C_1 symmetry. The two phenyl rings on each side of the heterocyclic ring system are twisted asymmetrically in opposite directions ("propeller type"): about 11.1° at the C10—C13 bond and about 14.2° at the C4—C7 bond as in the case of *tert*-butylphenyl derivative (TB-DPP) [6] and biphenyl derivative (BP-DPP) [8]. On the other hand, the twisting of the phenyl rings takes place in the same direction in other DPPs (C_i symmetry) [4,5,7]. In addition, the heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of 177.7° as in TB-DPP and BP-DPP, while it is completely planar in other DPPs. Due to this deformed structure, a slight dipole moment of about 0.16 D appears perpendicular to the molecular plane. The molecules are stacked in a "bricks in a brick wall" fashion as in BP-DPP. On the (a,c) molecular plane, 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 bond network as found in all DPP pigments [4-8] and causes the very good thermal and solvent resistance of the hydrogen bonded DPP pigments.

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Table 1. Data collection and handling.

Crystal:	red platelet, size 0.10 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	0.91 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 44 frames, $\Delta\omega = 5°$
$2\theta_{max}$:	50.0°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6787, 2613
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1300
$N(param)_{refined}$:	235
Programs:	SHELXS-86 [9], teXsan [10], ORTEPII [11]

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

Atom	Site	x	y	z	U_{iso}
H(1)	2*i*	0.3143	0.3014	1.3736	0.045
H(2)	2*i*	0.2137	0.0395	1.3158	0.048
H(3)	2*i*	0.2051	0.0558	1.1874	0.038
H(4)	2*i*	0.3616	0.6063	1.1750	0.044
H(5)	2*i*	0.3873	0.5763	1.3025	0.042
H(6)	2*i*	0.2442	-0.1367	0.9432	0.029
H(7)	2*i*	0.2664	0.6330	1.0624	0.034
H(8)	2*i*	0.2805	-0.1166	0.8246	0.035

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	2*i*	0.2767	–0.0924	0.6964	0.039
H(10)	2*i*	0.1393	0.4645	0.6962	0.036
H(11)	2*i*	0.1557	0.4439	0.8227	0.040
H(12)	2*i*	0.1304	–0.0610	0.5823	0.048
H(13)	2*i*	0.3680	–0.0316	0.5754	0.048
H(14)	2*i*	0.2325	0.0409	0.5098	0.048

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(15)	2*i*	0.4943	0.2754	0.5766	0.055
H(16)	2*i*	0.3574	0.3473	0.5113	0.055
H(17)	2*i*	0.3441	0.4508	0.5841	0.055
H(18)	2*i*	–0.0124	0.3015	0.5205	0.047
H(19)	2*i*	–0.0387	0.4065	0.5930	0.047
H(20)	2*i*	–0.1143	0.2017	0.5934	0.047

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	0.2616(5)	–0.1269(5)	1.0852(2)	0.045(2)	0.020(2)	0.029(2)	0.003(2)	–0.001(2)	–0.001(2)
O(2)	2*i*	0.2368(5)	0.6223(5)	0.9189(2)	0.036(2)	0.023(2)	0.025(2)	–0.005(2)	–0.004(2)	–0.004(2)
N(1)	2*i*	0.2444(6)	–0.0158(6)	0.9621(2)	0.037(3)	0.011(3)	0.026(2)	–0.005(2)	–0.001(2)	–0.007(2)
N(2)	2*i*	0.2593(6)	0.5128(6)	1.0434(2)	0.028(2)	0.024(3)	0.033(3)	–0.003(2)	0.003(2)	–0.005(2)
C(1)	2*i*	0.3045(9)	0.3091(9)	1.3208(3)	0.042(4)	0.039(4)	0.031(3)	–0.003(3)	–0.005(3)	–0.002(3)
C(2)	2*i*	0.2468(9)	0.154(1)	1.2864(3)	0.043(4)	0.046(4)	0.029(3)	0.006(3)	0.000(3)	0.001(3)
C(3)	2*i*	0.2378(8)	0.1651(8)	1.2106(3)	0.034(3)	0.026(3)	0.035(3)	–0.004(2)	0.003(2)	–0.008(3)
C(4)	2*i*	0.2748(7)	0.3311(8)	1.1668(3)	0.027(3)	0.021(3)	0.034(3)	–0.004(2)	–0.001(2)	–0.005(3)
C(5)	2*i*	0.3327(8)	0.4893(9)	1.2032(3)	0.037(3)	0.044(4)	0.029(3)	–0.001(3)	–0.003(2)	–0.001(3)
C(6)	2*i*	0.3465(8)	0.4708(9)	1.2786(3)	0.035(3)	0.035(4)	0.035(3)	0.000(3)	–0.002(3)	–0.005(3)
C(7)	2*i*	0.2637(7)	0.3454(7)	1.0865(3)	0.028(3)	0.007(3)	0.029(3)	0.001(2)	0.005(2)	0.000(2)
C(8)	2*i*	0.2514(7)	0.2078(7)	1.0396(3)	0.025(3)	0.016(3)	0.035(3)	–0.002(2)	0.002(2)	–0.002(3)
C(9)	2*i*	0.2540(7)	0.0085(8)	1.0363(3)	0.024(3)	0.021(3)	0.031(3)	0.000(2)	0.005(2)	–0.012(3)
C(10)	2*i*	0.2351(7)	0.1520(7)	0.9173(3)	0.026(3)	0.016(3)	0.027(3)	–0.008(2)	–0.004(2)	0.000(2)
C(11)	2*i*	0.2387(8)	0.2900(7)	0.9650(3)	0.032(3)	0.013(3)	0.028(3)	–0.002(2)	0.000(2)	–0.002(2)
C(12)	2*i*	0.2431(7)	0.4873(8)	0.9680(3)	0.023(3)	0.023(4)	0.031(3)	0.002(2)	–0.004(2)	–0.012(3)
C(13)	2*i*	0.2237(7)	0.1610(8)	0.8370(3)	0.023(3)	0.027(4)	0.030(3)	–0.003(2)	–0.003(2)	–0.003(3)
C(14)	2*i*	0.2547(8)	0.0037(8)	0.7983(3)	0.042(3)	0.019(3)	0.025(3)	0.001(2)	–0.003(2)	–0.002(2)
C(15)	2*i*	0.2486(8)	0.0183(8)	0.7221(3)	0.037(3)	0.022(3)	0.039(3)	0.001(2)	0.002(3)	–0.003(3)
C(16)	2*i*	0.2041(8)	0.1852(9)	0.6812(3)	0.027(3)	0.042(4)	0.025(3)	–0.005(3)	0.008(2)	–0.009(3)
C(17)	2*i*	0.1700(8)	0.3448(8)	0.7221(3)	0.036(3)	0.029(3)	0.024(3)	–0.001(2)	–0.004(2)	–0.001(2)
C(18)	2*i*	0.1795(9)	0.3329(9)	0.7969(3)	0.047(4)	0.025(3)	0.029(3)	–0.001(3)	–0.001(3)	–0.012(3)
C(19)	2*i*	0.2004(8)	0.2089(9)	0.5956(3)	0.036(3)	0.036(4)	0.030(3)	0.005(3)	–0.001(2)	–0.015(3)
C(20)	2*i*	0.2361(9)	0.0222(9)	0.5628(3)	0.052(4)	0.043(4)	0.026(3)	–0.004(3)	–0.004(3)	–0.006(3)
C(21)	2*i*	0.363(1)	0.331(1)	0.5642(3)	0.056(4)	0.061(5)	0.024(3)	–0.024(3)	0.005(3)	–0.015(3)
C(22)	2*i*	–0.0108(9)	0.2869(9)	0.5736(3)	0.058(4)	0.035(4)	0.023(3)	0.006(3)	–0.006(3)	–0.007(3)

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