Refinement of the crystal structure of α-1,4-dioxo-3,6-diphenylpyrrolo-[3,4-*c*]pyrrole-2,5(1*H*,4*H*)-dicarboxylic acid bis(1,1-dimethylethyl) ester, $C_{28}H_{28}N_2O_6$

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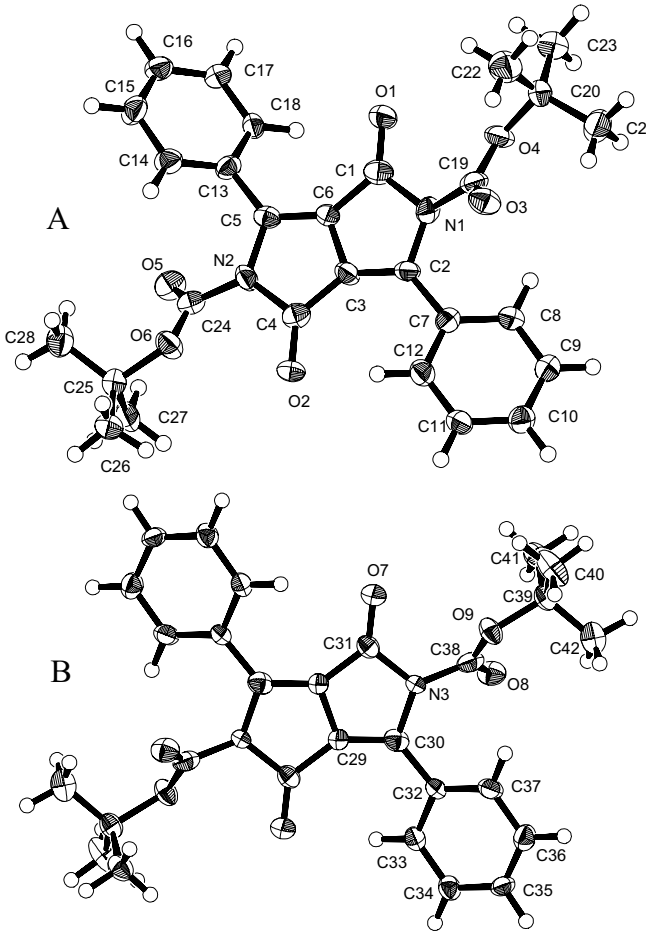

Abstract

$C_{28}H_{28}N_2O_6$, monoclinic, $P12_1/n1$ (No. 14), a = 10.437(2) Å, b = 21.367(4) Å, c = 16.799(3) Å, β = 94.64(1)°, V = 3734.0 Å^3, Z = 6, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.071, T = 93 K.

Source of material

The title compound was prepared according to the methode previously reported in [1]. The single crystals were then recrystallized from acetonitrile.

Discussion

The title compound hereafter called *t*-BOC DPP is a soluble, yellowish precursor ("latent pigment") [1,2] of diketopyrrolopyrrole (DPP) [3] that is known as an industrially important red pigment. The soluble precursor is prepared by replacing the H atom of the NH group with a *t*-butoxycarbonyl (*t*-BOC) group. The insoluble parent DPP can then be regenerated by thermo-chemical treatment of the precursor. The present "latent pigment technology" is a versatile and promising technique for the preparation of nano pigment particles as well as transparent pigmented thin films, etc. The crystal structure of the parent DPP has previously been reported by us [4]. In regard to the structure of *t*-BOC DPP, MacLean and others reported that there exist two crystal modifications (α & β) and presented the structure of the α form as obtained by Rietveld refinement from powder X-ray diffraction data as well as the β form solved directly from powder X-ray diffraction data using their Monte Carlo technique and Rietveld refinement [5]. Our structure report here deals with the full structure analysis of the α form. The structure of the β form will shortly be reported elsewhere.

The title compound crystallizes with one and half molecules (A and B, respectively, see figure) in the asymmetric unit. Molecule A resides on a general position while molecule B is on a symmetry center. There are 6 molecules in the unit cell (four of molecule A and two of molecule B). The phenyl rings of molecule A are asymmetrically deviated, in the same direction, from the heterocyclic system by 26.1° ({C1N1C2C3C6}/{C7C8C9C10C11C12}) and 42.3° ({C3C4N2C5C6}/{C13C14C15C16C17C18}). The *t*-BOC groups attached to the N atom of the heterocyclic ring are also twisted in the same direction with respect to the heterocyclic system by 46.0° ({O3O4C19N1}/{C1C2C3C6N1}) and 40.0° ({N2O5O6C24}/{N2C3C4C5C6}). Furthermore, the heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of about 179.7°. On the other hand, in molecule B, the phenyl rings are symmetrically twisted in the same direction by 25.3° due to *Ci* symmetry and the torsion angle of the *t*-BOC group is 55.3°. The molecules of both conformations are stacked along the *a* axis in the sequence of A-A-B-A-A-B- in a fashion "herringbone". The present result is basically in good agreement with previous studies [5], although all torsion angles are slightly different and the sequence of the molecular stack is described as A-B-A-B- in that report.

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Table 1. Data collection and handling.

Crystal:	yellow platelet, size 0.10 × 0.20 × 0.20 mm
Wavelength:	Cu K_α radiation (1.5419 Å)
μ:	7.58 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, 72 frames, $\Delta\omega = 10°$
$2\theta_{max}$:	135°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	32175, 6577
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1810
$N(param)_{refined}$:	487
Programs:	SHELXS-86 [6], teXsan [7], ORTEP-III [8], ABSCOR [9]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.1601	0.6148	0.5991	0.043
H(2)	4*e*	0.3681	0.6302	0.5540	0.049
H(3)	4*e*	0.5524	0.6127	0.6418	0.049
H(4)	4*e*	0.5341	0.5748	0.7724	0.045
H(5)	4*e*	0.3267	0.5577	0.8180	0.043
H(6)	4*e*	–0.1739	0.4556	0.9967	0.044
H(7)	4*e*	–0.3849	0.4339	1.0317	0.049
H(8)	4*e*	–0.5599	0.4270	0.9327	0.048
H(9)	4*e*	–0.5207	0.4365	0.7965	0.045
H(10)	4*e*	–0.3123	0.4601	0.7589	0.040
H(11)	4*e*	0.0136	0.7605	0.5832	0.056
H(12)	4*e*	–0.0534	0.7326	0.5054	0.056
H(13)	4*e*	–0.0916	0.7986	0.5339	0.056
	4*e*	–0.1144	0.7693	0.7084	0.063
H(15)	4*e*	–0.2200	0.8076	0.6598	0.063
H(16)	4*e*	–0.2561	0.7467	0.7031	0.063
H(17)	4*e*	–0.3291	0.7515	0.5270	0.056
H(18)	4*e*	–0.2732	0.6870	0.5050	0.056
H(19)	4*e*	–0.3512	0.6933	0.5794	0.059
H(20)	4*e*	0.3219	0.3365	1.1187	0.056
H(21)	4*e*	0.3479	0.3787	1.0466	0.060
H(22)	4*e*	0.2669	0.4040	1.1131	0.060
H(23)	4*e*	0.1163	0.2777	0.9484	0.050
H(24)	4*e*	0.2596	0.2974	0.9505	0.050
H(25)	4*e*	0.2149	0.2513	1.0140	0.050
H(26)	4*e*	0.0458	0.3676	1.1237	0.048
H(27)	4*e*	–0.0213	0.3232	1.0602	0.048
H(28)	4*e*	0.0780	0.2967	1.1253	0.048
H(29)	4*e*	0.1917	–0.0195	0.0619	0.039
H(30)	4*e*	–0.0189	0.0152	0.0880	0.043
H(31)	4*e*	–0.0514	0.1206	0.1208	0.040
H(32)	4*e*	0.1234	0.1921	0.1379	0.047
H(33)	4*e*	0.3319	0.1567	0.1116	0.046
H(34)	4*e*	0.7954	0.2407	0.1277	0.067
H(35)	4*e*	0.6690	0.2791	0.1160	0.067
H(36)	4*e*	0.7646	0.2910	0.1901	0.067
H(37)	4*e*	0.7090	0.1389	0.2822	0.040
H(38)	4*e*	0.8225	0.1583	0.2333	0.040
H(39)	4*e*	0.7839	0.2003	0.3027	0.040
H(40)	4*e*	0.5736	0.2648	0.2834	0.067
H(41)	4*e*	0.4901	0.2599	0.2029	0.067
H(42)	4*e*	0.4951	0.2045	0.2628	0.067

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)	4*e*	–0.2383(2)	0.5801(1)	0.7230(1)	0.029(2)	0.044(2)	0.045(2)	0.003(1)	–0.001(1)	0.009(1)
O(2)	4*e*	0.2380(2)	0.4625(1)	0.8668(1)	0.023(2)	0.047(2)	0.041(2)	0.006(1)	–0.003(1)	0.006(1)
O(3)	4*e*	0.0531(2)	0.6957(1)	0.7018(1)	0.035(2)	0.038(2)	0.050(2)	0.000(2)	–0.007(2)	–0.001(2)
O(4)	4*e*	–0.1241(2)	0.6629(1)	0.6257(1)	0.026(2)	0.035(2)	0.052(2)	0.006(2)	–0.002(1)	0.008(2)
O(5)	4*e*	–0.0503(2)	0.3531(1)	0.9214(1)	0.037(2)	0.041(2)	0.046(2)	–0.008(2)	0.001(1)	–0.005(2)
O(6)	4*e*	0.1259(2)	0.3989(1)	0.9852(1)	0.037(2)	0.040(2)	0.039(2)	–0.001(2)	–0.008(1)	0.009(2)
O(7)	4*e*	0.7388(2)	0.0657(1)	0.0584(1)	0.027(2)	0.040(2)	0.049(2)	–0.005(2)	0.001(1)	–0.009(1)
O(8)	4*e*	0.5071(2)	0.0992(1)	0.2140(1)	0.033(2)	0.049(2)	0.032(2)	–0.007(1)	0.008(1)	0.005(2)
O(9)	4*e*	0.6086(2)	0.1652(1)	0.1346(1)	0.043(2)	0.029(2)	0.030(2)	–0.012(1)	0.005(1)	–0.003(1)
N(1)	4*e*	–0.0161(3)	0.5933(1)	0.7050(2)	0.032(2)	0.023(2)	0.040(2)	–0.008(2)	0.008(2)	0.005(2)
N(2)	4*e*	0.0176(3)	0.4517(1)	0.8860(2)	0.034(2)	0.031(2)	0.035(2)	0.001(2)	–0.001(2)	0.013(2)
N(3)	4*e*	0.5219(3)	0.0776(1)	0.0809(2)	0.020(2)	0.030(2)	0.035(2)	–0.002(2)	–0.001(2)	–0.012(2)
C(1)	4*e*	–0.1259(4)	0.5653(2)	0.7400(2)	0.031(3)	0.034(3)	0.039(3)	0.001(2)	–0.002(2)	–0.005(2)
C(2)	4*e*	0.0998(4)	0.5672(2)	0.7392(2)	0.021(2)	0.033(3)	0.041(3)	0.005(2)	0.002(2)	0.006(2)
C(3)	4*e*	0.0690(4)	0.5244(2)	0.7942(2)	0.026(3)	0.032(3)	0.035(3)	0.001(2)	–0.004(2)	0.008(2)
C(4)	4*e*	0.1259(4)	0.4785(2)	0.8494(2)	0.027(3)	0.035(3)	0.036(3)	–0.004(2)	0.000(2)	–0.006(2)
C(5)	4*e*	–0.0996(4)	0.4760(2)	0.8504(2)	0.029(3)	0.028(3)	0.028(3)	0.006(2)	–0.002(2)	–0.007(2)
C(6)	4*e*	–0.0669(4)	0.5202(2)	0.7961(2)	0.028(3)	0.024(3)	0.031(3)	0.006(2)	0.004(2)	0.002(2)
C(7)	4*e*	0.2251(4)	0.5835(2)	0.7120(2)	0.031(3)	0.027(3)	0.034(3)	–0.001(2)	0.007(2)	–0.001(2)
C(8)	4*e*	0.2378(3)	0.6052(2)	0.6350(2)	0.029(3)	0.036(3)	0.034(3)	0.004(2)	0.000(2)	0.002(2)
C(9)	4*e*	0.3596(4)	0.6156(2)	0.6094(2)	0.034(3)	0.047(3)	0.037(3)	0.000(2)	0.006(2)	0.006(2)
C(10)	4*e*	0.4673(4)	0.6046(2)	0.6604(2)	0.036(3)	0.032(3)	0.044(3)	–0.003(2)	0.007(2)	0.003(2)
C(11)	4*e*	0.4565(4)	0.5835(2)	0.7366(2)	0.030(3)	0.038(3)	0.041(3)	0.004(2)	–0.001(2)	0.008(2)
C(12)	4*e*	0.3354(4)	0.5723(2)	0.7627(2)	0.042(3)	0.033(3)	0.033(3)	0.007(2)	0.005(2)	0.004(2)
C(13)	4*e*	–0.2267(4)	0.4590(2)	0.8741(2)	0.029(3)	0.027(3)	0.043(3)	0.000(2)	0.011(2)	0.003(2)
C(14)	4*e*	–0.2456(4)	0.4510(2)	0.9540(2)	0.031(3)	0.048(3)	0.032(3)	0.004(2)	0.001(2)	–0.005(2)
C(15)	4*e*	–0.3707(4)	0.4399(2)	0.9752(2)	0.038(3)	0.056(3)	0.029(3)	–0.003(3)	0.009(2)	–0.002(2)
C(16)	4*e*	–0.4713(3)	0.4343(2)	0.9167(2)	0.026(3)	0.040(3)	0.048(3)	0.000(2)	0.006(2)	0.005(2)
C(17)	4*e*	–0.4495(4)	0.4413(2)	0.8377(2)	0.027(3)	0.044(3)	0.042(3)	0.001(2)	0.006(2)	0.006(2)
C(18)	4*e*	–0.3274(4)	0.4530(2)	0.8148(2)	0.029(2)	0.036(3)	0.030(2)	–0.001(2)	0.001(2)	0.011(2)
C(19)	4*e*	–0.0240(4)	0.6567(2)	0.6774(2)	0.023(3)	0.047(3)	0.034(3)	0.005(2)	0.005(2)	–0.003(3)
C(20)	4*e*	–0.1672(4)	0.7269(2)	0.6001(2)	0.037(3)	0.041(3)	0.041(3)	0.003(2)	0.007(2)	0.015(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(21)	4*e*	–0.0678(4)	0.7566(2)	0.5527(2)	0.054(3)	0.054(3)	0.048(3)	–0.002(3)	0.017(2)	0.007(3)
C(22)	4*e*	–0.1916(4)	0.7655(2)	0.6733(2)	0.062(3)	0.048(3)	0.054(3)	0.014(3)	0.008(3)	–0.002(2)
C(23)	4*e*	–0.2884(4)	0.7135(2)	0.5504(2)	0.040(3)	0.056(3)	0.049(3)	0.006(3)	0.002(2)	0.005(2)
C(24)	4*e*	0.0256(4)	0.3953(2)	0.9321(2)	0.031(3)	0.039(3)	0.039(3)	0.006(2)	0.009(2)	–0.001(3)
C(25)	4*e*	0.1632(4)	0.3430(2)	1.0364(2)	0.036(3)	0.042(3)	0.035(3)	0.001(3)	0.007(2)	0.008(2)
C(26)	4*e*	0.2851(4)	0.3667(2)	1.0820(2)	0.030(3)	0.068(3)	0.046(3)	0.006(2)	–0.001(2)	0.017(3)
C(27)	4*e*	0.1911(4)	0.2881(2)	0.9843(2)	0.060(3)	0.045(3)	0.038(3)	0.017(3)	0.009(2)	0.017(2)
C(28)	4*e*	0.0599(4)	0.3315(2)	1.0907(2)	0.054(3)	0.044(3)	0.037(3)	0.000(3)	0.009(2)	0.002(2)
C(29)	4*e*	0.4334(3)	–0.0008(2)	0.0075(2)	0.025(2)	0.025(2)	0.030(2)	0.000(2)	0.002(2)	–0.003(2)
C(30)	4*e*	0.4062(4)	0.0450(2)	0.0596(2)	0.031(3)	0.023(3)	0.038(3)	–0.004(2)	–0.001(2)	0.005(2)
C(31)	4*e*	0.6268(4)	0.0492(2)	0.0438(2)	0.032(3)	0.025(3)	0.029(3)	–0.004(2)	0.000(2)	0.000(2)
C(32)	4*e*	0.2809(4)	0.0666(2)	0.0842(2)	0.025(2)	0.028(3)	0.031(2)	–0.005(2)	0.001(2)	–0.007(2)
C(33)	4*e*	0.1773(4)	0.0245(2)	0.0775(2)	0.035(3)	0.027(3)	0.028(3)	0.000(2)	–0.001(2)	–0.003(2)
C(34)	4*e*	0.0535(4)	0.0455(2)	0.0918(2)	0.036(3)	0.026(3)	0.036(3)	–0.004(2)	0.004(2)	–0.002(2)
C(35)	4*e*	0.0363(3)	0.1058(2)	0.1131(2)	0.020(2)	0.045(3)	0.032(3)	0.005(2)	0.001(2)	–0.003(2)
C(36)	4*e*	0.1357(4)	0.1485(2)	0.1207(2)	0.039(3)	0.032(3)	0.035(3)	0.008(2)	0.002(2)	–0.002(2)
C(37)	4*e*	0.2589(4)	0.1276(2)	0.1062(2)	0.027(2)	0.034(3)	0.039(3)	–0.005(2)	–0.004(2)	–0.003(2)
C(38)	4*e*	0.5451(4)	0.1147(2)	0.1517(3)	0.022(3)	0.034(3)	0.048(3)	0.003(2)	0.002(2)	0.005(3)
C(39)	4*e*	0.6573(4)	0.2090(2)	0.2015(2)	0.039(3)	0.024(3)	0.033(3)	–0.005(2)	0.001(2)	0.000(2)
C(40)	4*e*	0.7251(4)	0.2583(2)	0.1568(2)	0.086(4)	0.049(3)	0.040(3)	–0.028(3)	–0.004(3)	–0.004(2)
C(41)	4*e*	0.7494(4)	0.1738(2)	0.2579(2)	0.043(3)	0.041(3)	0.029(3)	–0.009(2)	0.003(2)	–0.003(2)
C(42)	4*e*	0.5459(4)	0.2359(2)	0.2396(2)	0.060(3)	0.053(3)	0.054(3)	0.000(3)	0.005(3)	–0.018(3)

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