

The β -form of di-*tert*-butyl 1,4-dioxo-3,6-diphenyl-1,2,4,5-tetrahydropyrrolo-[3,4-*c*]pyrrole-2,5-dicarboxylate

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Key indicators

Single-crystal X-ray study

$T = 93\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$

R factor = 0.058

wR factor = 0.125

Data-to-parameter ratio = 13.5

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

The title compound, $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_6$, is a soluble precursor ('latent pigment') of diketopyrrolopyrrole pigments. The molecules are stacked along the a axis in a parallel arrangement. The present structure of the β -form is quite different from that of the previously reported α -form [MacLean *et al.* (2000). *J. Chem. Soc. Perkin Trans. 2*, pp. 1513–1519].

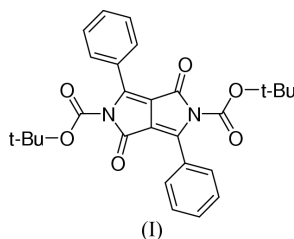
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Comment

The title compound, (I), is a soluble yellow precursor ('latent pigment') (Zambounis *et al.*, 1994, 1997) of diketopyrrolopyrrole pigments (DPP) (Herbst & Hunger, 1997); it is known as an industrially important red pigment. The soluble precursor is prepared by replacing the H atom of the NH group with a *tert*-butoxycarbonyl (*t*-BOC) group, hereafter called *t*-BOC DPP. The insoluble parent DPP can then be regenerated by thermochemical 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 (Mizuguchi *et al.*, 1992). In regard to the structure of *t*-BOC DPP, MacLean *et al.* (2000) reported that there exist two crystal modifications (α and 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. We have reported previously the structure of the α -form based on the full single-crystal structural analysis (Mizuguchi, 2003). Our report here deals with the full structure analysis of the β form, (I).



The title compound crystallizes in space group $P2_1/c$ with four equivalent molecules, devoid of symmetry, in the unit cell. An *ORTEP*III (Burnett & Johnson, 1996) plot is shown in Fig. 1. The phenyl rings are twisted in opposite directions from the heterocyclic system by $34.3(1)^\circ$ (N1/C1/C2/C5/C6 and C7–C12) and $29.3(1)^\circ$ (N2/C2–C5 and C15–C20). The *t*-BOC groups attached to the N atom of the heterocyclic ring

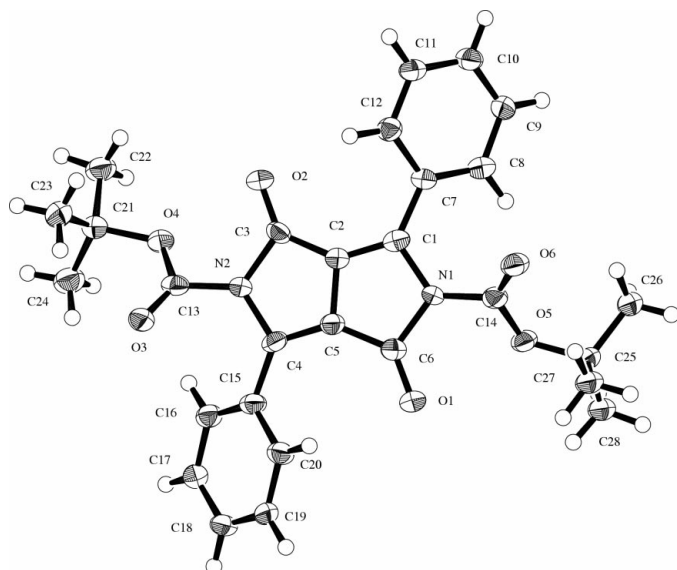


Figure 1
A view of the molecular structure of (I), showing ellipsoids at the 50% probability level for non-H atoms.

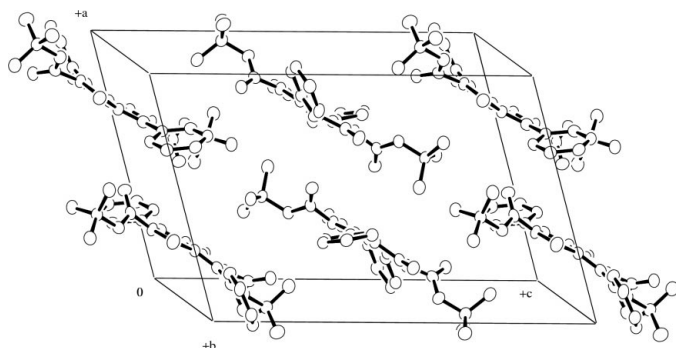


Figure 2
Packing structure of the β -form of (I).

are also twisted in opposite directions with respect to the heterocyclic system by $45.3(1)^\circ$ (N1/C14/O5/O6 and N1/C1/C2/C5/C6) and $41.5(1)^\circ$ (N2/C13/O3/O4 and N2/C2-C5). Furthermore, the heterocyclic ring system is not entirely planar but is folded about C2-C5, with a dihedral angle of $169.5(1)^\circ$. The molecules are stacked along the a axis in a parallel arrangement (Fig. 2). The present result is similar to, but still different from, the studies of MacLean *et al.* (2000) based on powder diffraction analysis. They assumed that the molecule has an inversion center, leading to space group $P2_1/c$ with $Z = 2$; the a axis [$6.2280(5) \text{ \AA}$] is half of our value [$a = 12.798(2) \text{ \AA}$; $P2_1/c$ with $Z = 4$].

Experimental

The title compound was prepared according to the method described in the literature (Zambounis *et al.*, 1994). The product was then dissolved in acetonitrile and single crystals [(I), β -form] were grown by slowly and completely evaporating the solvent over a period of a week. This slow solvent evaporation was the key to the successful growth of the β -form; crystals of the α -form were easily obtained by recrystallization from an acetonitrile solution in a closed system (Mizuguchi, 2003).

Crystal data

$C_{28}H_{28}N_2O_6$
 $M_r = 488.54$
Monoclinic, $P2_1/c$
 $a = 12.798(2) \text{ \AA}$
 $b = 10.466(1) \text{ \AA}$
 $c = 19.215(3) \text{ \AA}$
 $\beta = 108.10(1)^\circ$
 $V = 2446.5(6) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.326 \text{ Mg m}^{-3}$
Cu $K\alpha$ radiation
Cell parameters from 16 150 reflections
 $\theta = 3.6\text{--}68.2^\circ$
 $\mu = 0.77 \text{ mm}^{-1}$
 $T = 93.2 \text{ K}$
Prism, yellow-green
 $0.30 \times 0.20 \times 0.06 \text{ mm}$

Data collection

Rigaku R-Axis RAPID Imaging
Plate diffractometer
 ω scans; 48 frames, $\Delta\omega = 15^\circ$
Absorption correction: multi-scan (Higashi, 1995)
 $T_{\min} = 0.783$, $T_{\max} = 0.955$
21 098 measured reflections

4408 independent reflections
2190 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.060$
 $\theta_{\text{max}} = 67.8^\circ$
 $h = -15 \rightarrow 15$
 $k = -11 \rightarrow 12$
 $l = -23 \rightarrow 23$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.126$
 $S = 0.88$
4401 reflections
325 parameters

H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 1

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

| | | | |
|--------------|-------------|---------------|-------------|
| O1—C6 | 1.215 (4) | N2—C3 | 1.458 (4) |
| O2—C3 | 1.215 (4) | N2—C4 | 1.421 (4) |
| O3—C13 | 1.202 (4) | N2—C13 | 1.422 (5) |
| O4—C13 | 1.324 (4) | C1—C2 | 1.349 (5) |
| O4—C21 | 1.497 (5) | C1—C7 | 1.466 (5) |
| O5—C14 | 1.326 (4) | C2—C3 | 1.457 (5) |
| O5—C25 | 1.487 (5) | C2—C5 | 1.430 (4) |
| O6—C14 | 1.200 (4) | C4—C5 | 1.375 (5) |
| N1—C1 | 1.429 (4) | C4—C15 | 1.463 (5) |
| N1—C6 | 1.457 (4) | C5—C6 | 1.452 (5) |
| N1—C14 | 1.422 (5) | | |
| O3—C13—N2—C3 | $-133.2(3)$ | N1—C1—C7—C8 | $30.9(5)$ |
| O3—C13—N2—C4 | $32.4(4)$ | N1—C1—C7—C12 | $-152.0(3)$ |
| O4—C13—N2—C3 | $47.6(3)$ | N2—C4—C15—C16 | $25.0(4)$ |
| O4—C13—N2—C4 | $-146.8(3)$ | N2—C4—C15—C20 | $-159.1(3)$ |
| O5—C14—N1—C1 | $-145.1(3)$ | C2—C1—N1—C14 | $-165.6(3)$ |
| O5—C14—N1—C6 | $53.7(3)$ | C2—C1—C7—C8 | $-141.0(4)$ |
| O6—C14—N1—C1 | $34.1(4)$ | C5—C4—C15—C16 | $-146.3(3)$ |
| O6—C14—N1—C6 | $-127.2(3)$ | C5—C4—C15—C20 | $29.6(4)$ |

All H atoms were positioned geometrically, but not refined.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *TEXSAN*.

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