tert-Butyl 1,4-dioxo-3,6-diphenyl-1,2,4,5-tetrahydropyrrolo[3,4-c]-pyrrole-2-carboxylate

Yasuo Imura, Takatoshi Senju and Jin Mizuguchi
The title compound, C_{23}H_{20}N_{2}O_{4}, is a soluble precursor ('latent pigment') of diketopyrrolopyrrole pigments. The tert-butoxycarbonyl group is twisted by 78.5 (1)° with respect to the heterocyclic ring system. In the crystal structure, pairs of molecules form centrosymmetric dimers through N—H⋯O intermolecular hydrogen bonds and are stacked in a herringbone fashion along the a axis.

Comment

The title compound, (I), is a soluble precursor ('latent pigment') (Zambounis et al., 1994, 1997) of diketopyrrolopyrrole (DPP), an industrially important red pigment (Herbst & Hunger, 1993). The soluble precursor is prepared by replacing the H atom of the NH group by a tert-butoxycarbonyl (t-BOC) group. Both mono- and disubstituted t-BOC DPPs can be prepared. The former is called mono-BOC DPP while the latter is simply t-BOC DPP. The insoluble parent DPP can then be regenerated by thermal decomposition of the precursor at around 450 K. The present 'latent pigment technology' has recently attracted attention as a versatile and promising technique for the preparation of pigment nanoparticles as well as transparent thin films for electronic and imaging applications. The structure of t-BOC DPP has previously been published (MacLean et al., 2000; Mizuguchi, 2003a,b). The present paper reports the structure of mono-BOC DPP, (I).

The title compound is shown in Fig. 1. The phenyl rings deviate asymmetrically from the heterocyclic system in the same direction by 4.4 (1)° (N1/C1/C2/C5/C6 and C7/C8/C9/C10/C11/C12) and 9.3 (1)° (N2/C1/C2/C3/C4 and C13/C14/C15/C16/C17/C18). The t-BOC group attached to the N atom of the heterocyclic ring is twisted with respect to the heterocyclic system by 78.5 (1)° (N2/C1/C2/C3/C4 and O3/O4/C19/C20). Furthermore, the heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of 177.6 (1)° between the two five-membered rings. Fig. 2 shows...
the projection of the structure on to the $bc$ plane. In the crystal structure, pairs of molecules form centrosymmetric dimers through N—H···O intermolecular hydrogen bonds between the NH group of one molecule and the carbonyl group of a neighboring molecule. However, as shown in Fig. 3, there is a small step of about 0.84 Å between the two molecular planes of a centrosymmetric pair. The molecules are stacked in a herring-bone fashion along the $a$ axis.

**Experimental**

Mono-BOC DPP was prepared according to a method described in the literature (Zambounis et al., 1994). The product was purified by column chromatography. Single crystals of mono-BOC DPP were grown from a dichloromethane–ethyl acetate solution.

**Crystal data**

$\text{C}_{23}\text{H}_{20}\text{N}_{2}\text{O}_{4}$  
$M_r = 388.41$  
Monoclinic, $P2_1/n$  

$a = 6.0502 (6)$ Å  
$b = 16.524 (2)$ Å  
$c = 19.031 (2)$ Å  
$\beta = 95.744 (7)^\circ$  
$V = 1893.0 (4)$ Å$^3$  
$Z = 4$  

$D_1 = 1.363$ Mg m$^{-3}$  
Cu Kα radiation  

Cell parameters from 11787 reflections  
$\theta_{\text{min}} = 3.5–68.1^\circ$  
$\mu = 0.77$ mm$^{-1}$  
$T = 93.2$ K  
Needle, orange  

0.50 0.10 0.05 mm

**Data collection**

Rigaku R-AXIS RAPID imaging plate diffractometer  
$\omega$ scans  
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)  

R$_{\text{int}} = 0.052$  
$\theta_{\text{max}} = 68.3^\circ$  
$h = \pm 6 \rightarrow 6$  
$k = \pm 19 \rightarrow 19$  
l $= \pm 22 \rightarrow 22$

17683 measured reflections  
3329 independent reflections  
2370 reflections with $F^2 > 2\sigma(F^2)$

**Refinement**

Refinement on $F^2$  
$R[F^2 > 2\sigma(F^2)] = 0.051$  
$wR(F^2) = 0.141$  
$S = 1.08$  
3329 reflections  
265 parameters

H atoms treated by a mixture of independent and constrained refinement  

$\Delta\rho_{\text{max}} = 0.28$ e Å$^{-3}$  
$\Delta\rho_{\text{min}} = -0.31$ e Å$^{-3}$

**Table 1**

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—C5</td>
</tr>
<tr>
<td>N1—C6</td>
</tr>
<tr>
<td>N2—C3</td>
</tr>
<tr>
<td>N2—C4</td>
</tr>
<tr>
<td>C1—C2</td>
</tr>
<tr>
<td>C5—N1—C6</td>
</tr>
<tr>
<td>C3—N2—C4</td>
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<tr>
<td>C3—C1—C4</td>
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<tr>
<td>C5—C1—C5</td>
</tr>
<tr>
<td>C4—C1—C5</td>
</tr>
<tr>
<td>C1—C2—C3</td>
</tr>
</tbody>
</table>
Table 2
Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H · · · A</th>
<th>D—H</th>
<th>H · · · A</th>
<th>D · · · A</th>
<th>D—H · · · A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1—H1N1 · · · O1’</td>
<td>0.94 (2)</td>
<td>1.90 (2)</td>
<td>2.821 (2)</td>
<td>166 (2)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1 – x, 1 – y, 1 – z.

The H atom attached to the N atom was located in a difference density map and its coordinates were refined, with $U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(N)$. The remainder of the H atoms were positioned geometrically and included in a riding-model approximation with C–H = 0.95 Å and $U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(C)$.

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.

References