Polymorph of a Latent Pyrrolopyrrole Pigment: 1,4-Diketo-3,6-Diphenyl-Pyrrolo-[3,4-c]-Pyrrole

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Abstract

The title compound is a soluble precursor ("latent pigment") of diketopyrrolopyrrole pigment (DPP) that can be used for electronic and imaging applications. Two crystal forms (α & β) are known to exist in powders. Therefore, an attempt has been made in the present investigation to carry out full structure analysis on single crystals of both modifications. In the α-form, there are two independent molecules (A & B) characterized by C_1 and C_i symmetriesrespectively, and the space group $P2_1/n$. The molecules are stacked in the sequence of –A-A-B-A-A-B-… in a fashion "herringbone". On the other hand, the β-form crystallizes in the space group of $P2_1/c$ and the molecule belongs to C_1 symmetry. The molecules are stacked along the *a*-axis relative to each other in a parallel arrangement.

Introduction

The title compound is a soluble, yellowish precursor ("latent pigment")[1,2] of diketopyrrolopyrrole (DPP)[3] that is known as an industrially important red pigment (Fig. 1). The soluble precursor is prepared by replacing the H atom of the NH group with a *t*-butoxycarbonyl (*t*-BOC) group: hereafter called *t*-BOC DPP. The insoluble parent DPP can then be regenerated by thermal treatment of the precursor (Figs. 1 & 2). 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. used for electronic and imaging applications.

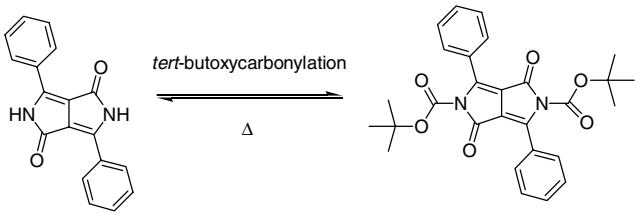

Figure 1. DPP and t-BOC DPP

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 and β forms based on single crystals.[6,7]

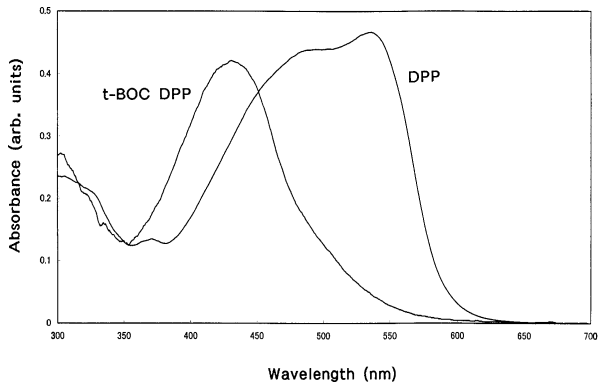

Figure 2. Diffuse reflectance spectra of DPP & t-BOC DPP.

Experimental

Preparation of Materials and Their Crystal Growth

t-BOC DPP was prepared according to the method previously reported in ref.1. Single crystals of the α form were obtained by recrystallization from an acetonitrile solution. On the other hand, single crystals of the β form were prepared by dissolving the product in acetonitrile, followed by slowly and completely evaporating the solvent over a period of a week.

Data Collection and Structure Analysis

The reflection data were collected by a Rigaku Diffractometer (model: Rapid F).[8] The both structures (α & β) were solved by direct methods using a program of SHELXS86.[9] Refinement was then made on F^2 by full-matrix least-squares calculations using the teXsan program package.[10]

Table 1. Crystallographic parameters of α and β forms for t -BOC DPP

	α-form		β-form	
	This work[1]	Simulation[2]	This work[3]	Simulation[2]
Formula	$C_{30}H_{32}N_2O_6$	$C_{30}H_{32}N_2O_6$	$C_{30}H_{32}N_2O_6$	$C_{30}H_{32}N_2O_6$
Molecular weight	516.59	516.59	516.59	516.59
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Spacegroup	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$
Molecular symmetry	C_1 & C_i	C_1 & C_i	C_1	C_i
a (Å)	10.437(2)	10.4851(4)	12.798(2)	6.2280(5)
b Å)	21.367(4)	21.4631(6)	10.466(1)	10.2981(2)
c (Å)	16.799(3)	17.1342(1)	19.215(3)	19.467(3)
β (°)	96.64	95.245(2)	108.10(1)	90.4605(8)
Z	6	6	4	2
R factor	0.071	0.077	0.058	0.079

Results and Discussion

Crystallographic Parameters

Table 1 shows the crystallographic parameters for the α & β modifications together with those of the simulations based on powder diffraction data.[5]

α-form

t-BOC DPP crystallizes with one and half molecules (A and B, respectively) in the asymmetric unit. Molecule A resides on a general position while molecule B is on a symmetry center. There are six molecules in the unit cell (four of molecule A and two of molecule B).

The ORTEP plots of molecules A and B are shown in Fig. 3. Molecules A and B belong to the point group of C_1 and C_i, respectively. 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 C_i symmetry and the torsion angle of the *t*-BOC group is 55.3°.

Figure 4 shows the molecular arrangement of the α form. 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 the studies of MacLean and others,[5] although all torsion angles are slightly different and the sequence of the molecular stack is described as A-B-A-B- in their report.

β-form

The title compound crystallizes in space group $P2_1/c$ with four non-centrosymmetric molecules: C_1.

The ORTEP plot is shown in Fig. 1. The phenyl rings are asymmetrically deviated, in opposite directions, from the heterocyclic system by 34.3° ({N1C1C2C5C6} / {C7C8C9C10C11C12}) and 29.3° ({N2C2C3C4C5} / {C15C16C17C18C19C20C}). The *t*-BOC groups attached to the N atom of the heterocyclic ring are also twisted in opposite directions with respect to the heterocyclic system by 45.3° ({N1C14O5O6} / {N1C1C2C5C6}) and 41.5° ({N2C13O3O4} / {N2C2C3C4C5}). Furthermore, the heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of about 169.5°.

Figure 6 shows the molecular arrangement of the β form. The molecules are stacked along the a-axis relative to each other in a parallel arrangement. The present result is similar but still different from the studies of MacLean et al based on powder diffraction analysis,[5] because they assumed that the molecule has an inversion center, leading to the space group of $P2_1/c$ with Z=2. Therefore, the *a* lattice (6.228 Å) is half of our value (a=12.798 Å; $P2_1/c$ with Z=4 in our case). The phenyl rings and *t*-BOC groups are symmetrically twisted with respect to the heterocyclic ring system and thus parallel to each other due to C_i symmetry. In addition, the heterocyclic ring system is entirely planar, not folded in the middle as in our case.

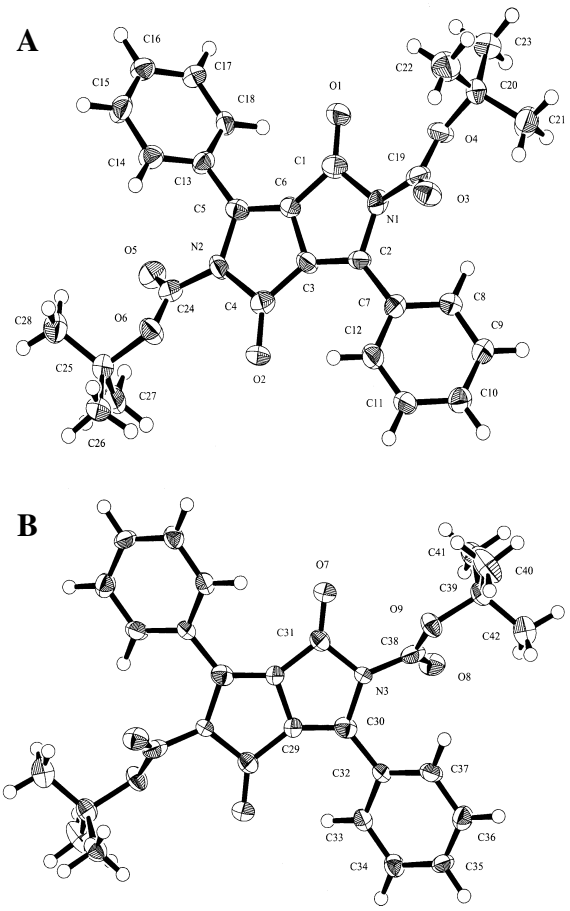

Figure 3. ORTEP plots of the α-form.

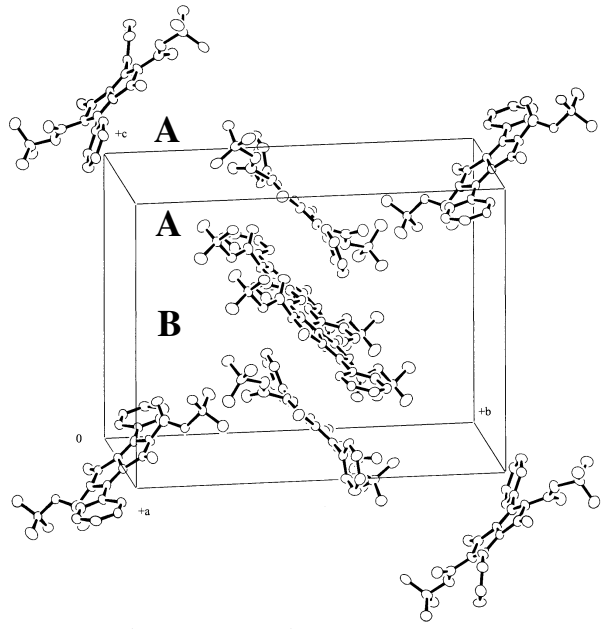

Figure 4. Molecular arrangement of the α-form.

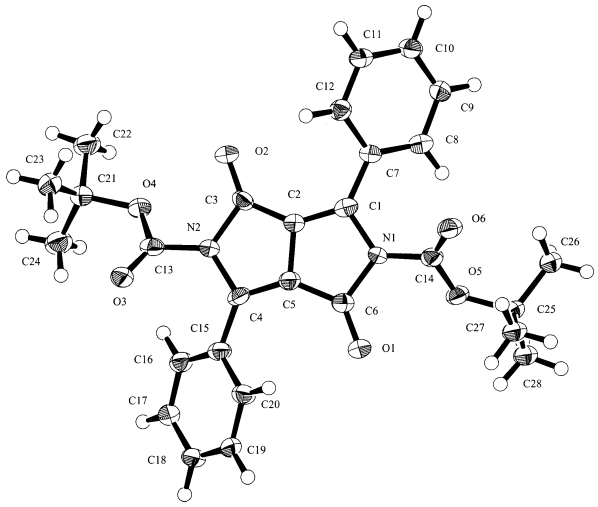

Figure 5. ORTEP plot of the β-form.

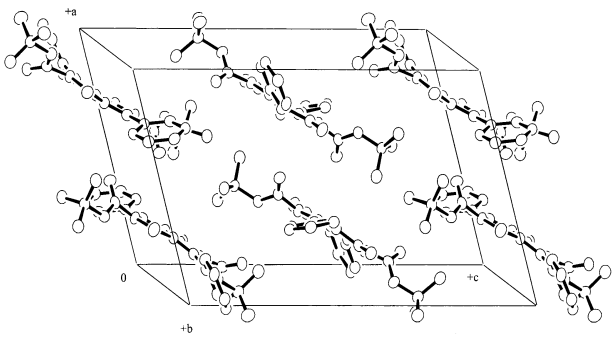

Figure 6. Molecular arrangement of the β-form.

Conclusions

The structure of the two crystal forms (α & β) of *t*-BOC DPP has been determined on the basis of the single crystals.

1. In the α-form, there are two independent molecules (A & B) characterized by C_1 and C_i symmetries respectively, and the space group $P2_1/n$. The molecules are stacked in the sequence of –A-A-B-A-A-B-… in a fashion "herringbone".
2. The β-form crystallizes in the space group of $P2_1/c$ and the molecule belongs to C_1 symmetry. The molecules are stacked along the *a*-axis relative to each other in a parallel arrangement.

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Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Sc. from the University of Tokyo in 1982 and Venia Docendi ("Habilitation") from the University of Bern in 1994. He worked at Sony Corporation Research Center from 1970 to 1985 and at Ciba-Geigy AG (Switzerland) from 1985 to 1995. During this time, he was mainly involved in research and development of photoconductors for laser printers as well as optical recording materials using organic pigments. He also gave a lecture on electronic devices and their materials at the University of Bern from 1994 to 1995. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science. His current interest is centered on the electronic characterization of organic pigments as viewed from exciton coupling effects as well as on the electronic applications of organic pigments.