A Pigment Precursor Based on *Mono t*-BOC Diketopyrrolopyrrole and its Thermal Regeneration into the Pigment

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Abstract

Pyrrolopyrroles (DPP) are industrially important red pigments in paint and imaging areas. The title compound is a soluble precursor of DPP called mono-BOC DPP ("latent pigment"), in which one of the NH groups in DPP is replaced by a t-*butoxycarbonyl (*t-*BOC) group to make it soluble in organic solvents. The regeneration and regenerated product of mono-BOC DPP have been studied in terms of thermogravimetric and X-ray diffraction analyses, as well as IR and diffuse reflectance spectra on powdered substances. Transformation from mono-BOC DPP to the parent DPP begins around 170°C and is completed around 220°C, accompanied by evolution of* CO_2*. The crystal phase of thermally regenerated DPP is different from that of DPP, although the diffuse reflectance spectrum of regenerated DPP on powder is quite similar to that of commercial one.*

Introduction

Pyrrolopyrroles (DPP) are industrially important red pigments in paint and imaging areas, characterized by NH···O intermolecular hydrogen bonds.[1] The title compound is a soluble precursor of DPP called mono-BOC DPP ("latent pigment": Fig. 1), in which one of the H atoms in two NH groups in DPP is replaced by a *t*-butoxycarbonyl (*t*-BOC) group to make DPP soluble in organic solvents. The background of the present study has already been set out in our previous paper.[2]

We have previously investigated the regeneration process of *t*-BOC DPP[3-5] and *t*-BOC quinacridone[2,6] as well as their crystal and electronic structure. *t*-BOC DPP has been thermally regenerated into DPP, however the color as well as the structure of regenerated DPP is slightly different from that of commercial one, and the heat and light stability is not as high as that of commercial product. In the present investigation, an attempt was made to transform mono-BOC DPP to DPP in the expectation that mono-BOC DPP ends up with DPP that corresponds to commercial DPP.

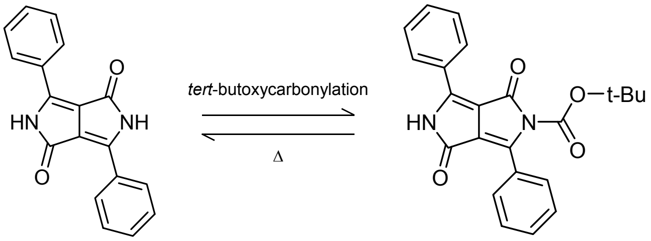

Figure 1. DPP, mono-BOC DPP and the regeneration process.

This paper deals with the crystal structure of mono-BOC DPP as well as its regeneration process to DPP.

Experiment

Preparation of Materials

Mono-BOC DPP was prepared according to the method described in the literature, using DPP obtained form CIBA Specialty Chemicals Inc.[7] The product was purified by column chromatography. Single crystals were then grown from a dichloromethane/ethylacetate solution.

Equipment

Diffuse reflectance spectra for powdered pigments were measured on a Shimadzu UV-2400PC spectrophotometer together with an integrating sphere attachment (ISR-240A from Shimadzu). The diffuse reflectance spectra were corrected by the Kubelka-Munk equation. Thermogravimetric analysis (TGA) was made on powdered samples at a heating rate of 5°C/min by means of a Rigaku Thermo Plus 8230. Powder X-ray diffraction diagrams were measured on a Rigaku diffractometer (model: Rapid F).

Regeneration Process

Powdered mono-BOC DPP was sandwiched between two thin slide glasses (thickness: 100 μm) and then placed on a hot plate. Regeneration from mono-BOC DPP to DPP was carried out at a heating rate of about 10°C. The following three samples were used for the study of the regeneration process: mono-BOC DPP at room temperature, orange/red powder heated at 170°C for 30 minutes and dull red sample heated at 220°C for 30 minutes.

Results and Discussion

Crystal Structure of Mono-BOC DPP[8]

Table 1 details the crystallographic parameters for mono-BOC DPP. Mono-BOC DPP crystallizes in space group $P2_1/n$ with four non-centro-symmetric molecules: C_1. Figure 2 shows the *ORTEP* plot. The phenyl rings are asymmetrically deviated 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/C17C18). 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 about 177.6(1)°.

Table 1: Crystallographic Parameters for Mono-BOC DPP

	Mono-BOC DPP
Formula	$C_{23}H_{20}N_2O_4$
Molecular weight	388.41
Crystal system	Monoclinic
Space group	$P2_1/n$
Molecular symmetry	C_1
a (Å)	6.0502(6)
b (Å)	16.524(2)
c(Å)	19.031(2)
β(Å)	95.744(7)
Z	4
R_1	0.051

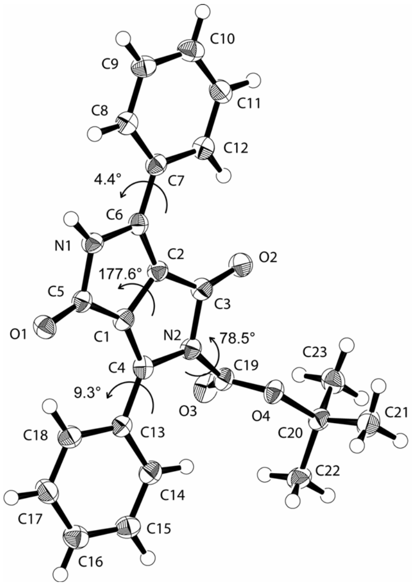

Figure 2. ORTEP plot of mono-BOC DPP.

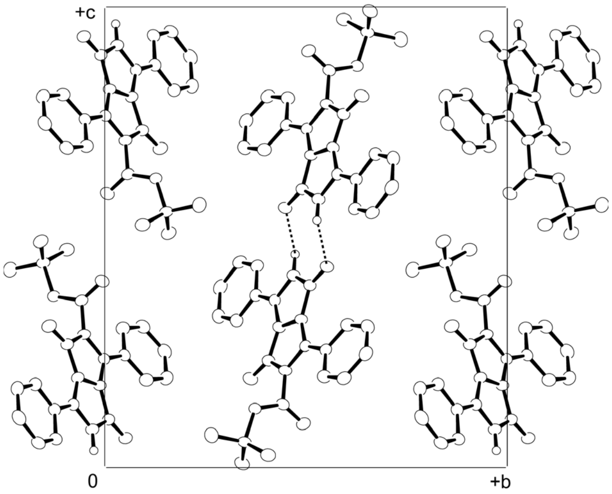

Figure 3. Projection onto the (b,c) plane.

Two molecules in the lattice are dimerized through NH···O intermolecular hydrogen bonds between the NH group of one molecule and the carbonyl group of the neighboring one (Fig. 3). However, there is a small step of about 0.84 Å between two molecular planes. The molecules are stacked in a "herringbone" fashion along the *a*-axis.

TGA Measurements

Figure 4 shows the TGA curves for the regeneration process from mono-BOC DPP as well as *t*-BOC DPP to DPP together with that of DPP. The weight loss begins to occur around 170°C and is completed around 220°C. The regeneration temperature of mono BOC DPP is about 30°C higher than that of *t*-BOC DPP. A weight loss of about 25% during this process corresponds exactly to the difference in molecular weight between mono-BOC DPP (M_w = 388.4) and DPP (M_w = 288.3). This indicates that the *t*-BOC group is completely eliminated and replaced by the H atom to form NH···O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one.

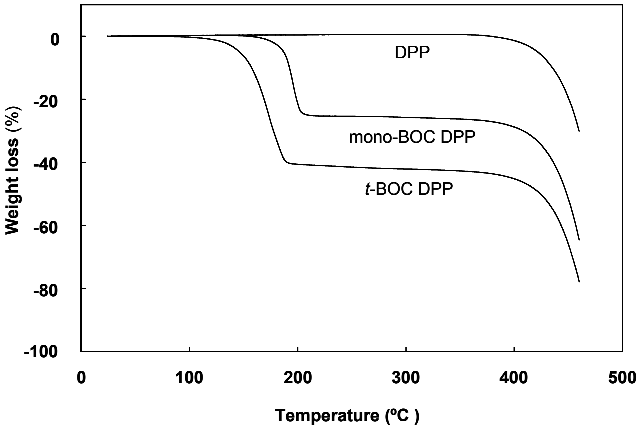

Figure 4. TGA curves measured on powdered mono-BOC, t-BOC and commercial DPPs.

IR Spectra

Figure 5 shows the change of the IR spectra of mono-BOC DPP at room temperature, 170 and 220°C together with the spectrum of commercial DPP. As shown in Fig. 3, there are NH···O hydrogen bonds between two molecules. One C=O group of mono-BOC DPP is hydrogen-bonded and the other remains free. There is also another C=O group in the t-BOC group. Our proposed assignment for NH, C=O and CH_3 groups is as follows. The broad band around 3280 cm^{-1} is assigned to the hydrogen-bonded NH stretching. The intensity of this band is increased due to the additional formation of NH···O hydrogen bonds caused by regeneration. The C=O stretching band in the t-BOC group is observed around 1750 cm^{-1}; while the free C=O stretching in the DPP skeleton appears as a small band around 1700 cm^{-1}.

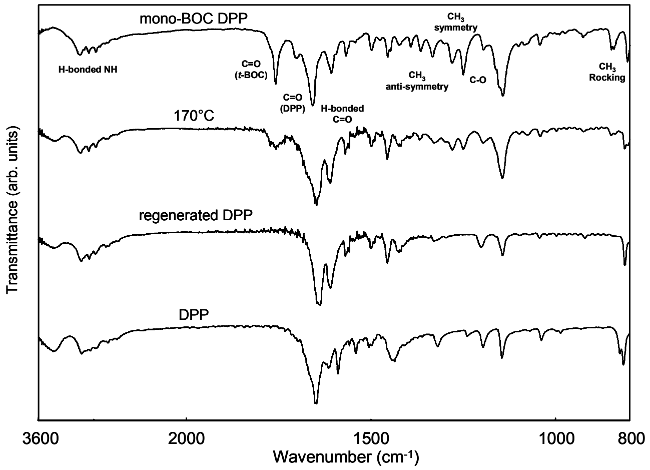

Figure 5. IR spectra of mono-BOC DPP treated at various temperatures.

On the other hand, the hydrogen-bonded C=O stretching bands are present around 1650 and 1610 cm^{-1} in the form of two split band. This is presumably due to a deformed structure of the dimer. The bands around 1370 and 1320 are assigned to the anti-symmetric deformation of the CH_3 group while the band around 1280 cm^{-1} is reduced to the symmetric deformation mode. The C-O stretching vibration and CH_3 rocking mode appear around 1240 and 840 cm^{-1}, respectively. At 170°C, the free C=O stretching band as well as the CH_3 characteristic bands begin to disappear. Instead, the NH stretching band is enhanced together with the hydrogen-bonded C=O stretching. Even at 220°C where the regeneration is complete, the two C=O stretching bands remain still separate, indicating that the molecule in the solid state is not entirely centrosymmetric as found in commercial DPP where only one single C=O stretching band is observed.[9] Additional difference bands are found at about 1440-1460 and 820 cm^{-1}.

Diffuse Reflectance Spectra

Figure 6 shows the diffuse reflectance spectra of mono-BOC DPP, regenerated DPP and commercial DPP. The shorter-wavelength band is more enhanced in DPP as compared with that of regenerated DPP. The reverse is the case in the longer-wavelength band. This is closely related to the fashion of molecular arrangement along the stacking axis.[10]

X-ray Diffraction Diagrams

Figure 7 shows the X-ray diffraction diagrams of mono-BOC DPP, intermediate state at 170°C and the final state at 220°C, together with that of commercial DPP. The diffraction peaks are assigned on the basis of the structure analysis.[8,9] Some peaks of regenerated DPP can successfully be attributed to those of DPP. However, the peaks denoted by arrows cannot be identified, indicating that the phase of regenerated DPP is different from that of DPP. Especially, significant deviations are recognized at higher angles. This might consequently cause a difference in absorption bands as shown in Fig. 6.

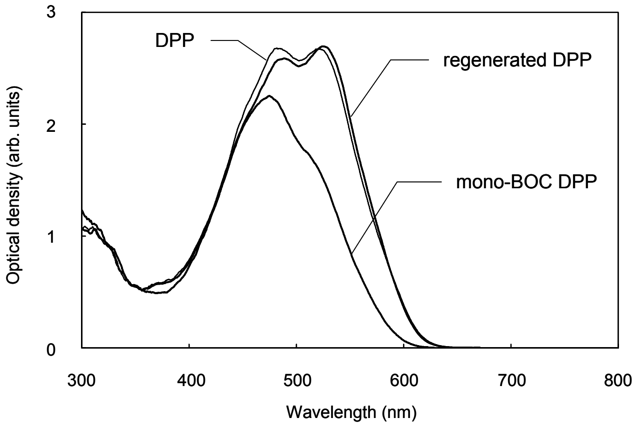

Figure 6. Diffuse reflectance spectra of the initial and final state of mono-BOC DPP together with commercial DPP.

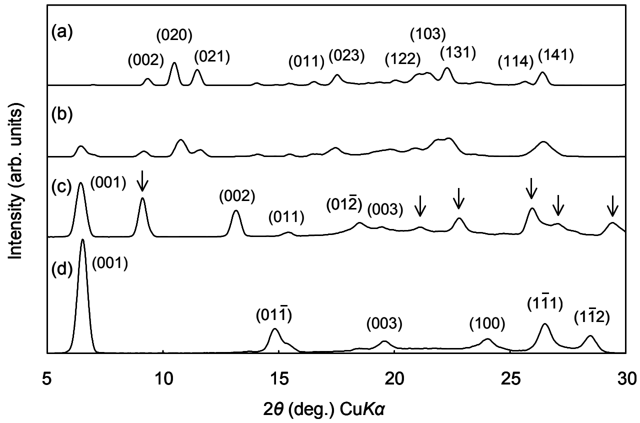

Figure 7. X-ray diffraction diagrams for (a) mono-BOC DPP, (b) intermediate state, (c) final state and (d) commercial DPP.

Conclusions

The conclusions drawn from the present investigation can be summarized as follows:

1. Mono-BOC DPP crystallizes in space group $P2_1/n$.
2. Transformation from mono-BOC DPP to DPP begins around 160°C and is completed around 220°C.
3. The phase of regenerated DPP is different from that of commercial DPP, although the absorption spectra are quite similar to each other.

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Author Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Science from the University of Tokyo in 1982 and Venia Docendi 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. Since 1995, Prof. Mizuguchi has been at Yokohama National University as professor of materials science.