

Polymorph of 1,4-diketo-3,6-dipyridyl-pyrrolo-[3,4-c]pyrrole

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Abstract

Diketopyrrolopyrroles (DPP) are well-known organic pigments. The title compound (DPPP) is one of DPP derivatives that shows a high proton affinity because of the N atoms of the pyridyl ring. Protonation at the N-site brings about a variety of changes in color as well as in electrical and photoelectrical conductivities. Two crystal modifications have been found to exist: DPPP I (grown from vapor phase) and DPPP II (grown from solution). Structure analysis revealed that there is a striking difference in intermolecular hydrogen bonds between two modifications: DPPP I is characterized only by NH...O hydrogen bonds whereas DPPP II include two of the H-bond based on NH...N and NH...O.

Introduction

Diketopyrrolopyrroles (for example DPP: Fig. 1(a)) are well-known organic pigments used not only for paint industries as well as in the imaging area.¹ DPPs have also attracted attention as a material useful for EL and color filters for LCD applications. The title compound (DPPP: Fig. 1(b)) is one of DPP derivatives that shows a high proton affinity because of the N atom of the pyridyl ring.

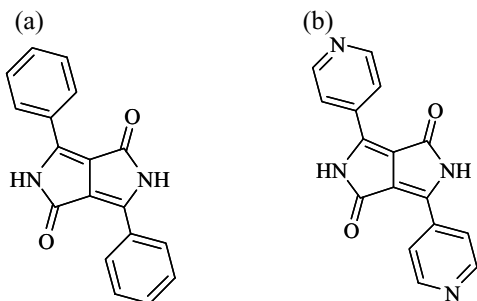


Figure 1. (a) DPP and (b) DPPP.

Protonation at the N-site (shown in the inset of Fig. 2) brings about a variety of changes in color as well as in electrical and photoelectrical conductivity.² For example, the absorption maximum is displaced from 560 to 580 nm due to

protonation by vapor of nitric acid as shown in Fig. 2, accompanied by a decrease in electrical resistivity by several orders of magnitude. The proton affinity is obviously a negative factor for colorants because the color change occurs quite early. This factor of DPPP is, however, useful for applications for acid and H₂ gas sensors.

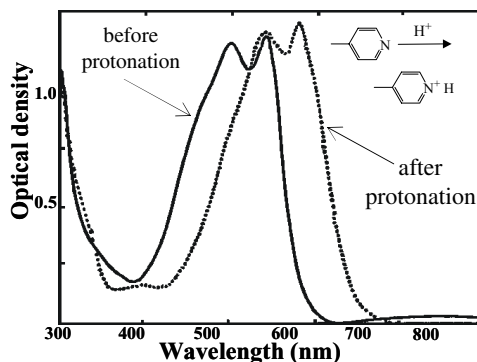


Figure 2. Solid-state spectra of evaporated DPPP before and after protonation.

In the course of our investigations on the sensor applications, we found that there are two phases, one of which shows a high proton affinity (phase I: grown from the vapor phase) and the other is quite insensitive to protons (phase II: recrystallized from solution). The structure of phase II has previously been reported.³ Therefore, the present investigation aims at elucidating the crystal structure of phase I.

Experiment

1. Sample Preparation and Crystal Growth

DPPP was synthesized according to the method described in Ref. 4 and purified six times by sublimation. Single crystals of DPPP I were then grown from the vapor phase in a closed system, using a two-zone furnace (Fig. 3). On the other hand, single crystals of DPPP II were grown by recrystallization from solution in *N,N*-dimethylacetamide using an autoclave (Taiatsu Co. Ltd.; model TPR-2).

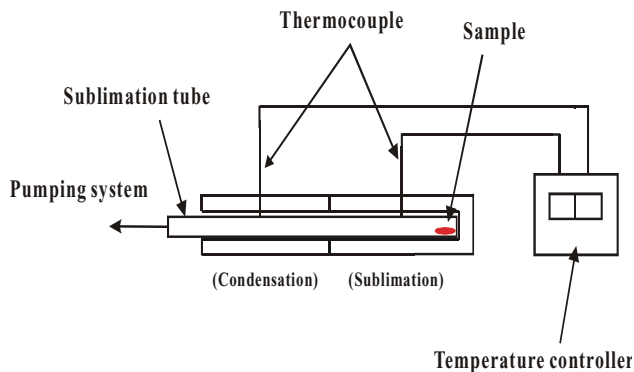


Figure 3. Apparatus for the crystal growth in a closed system.

2. Structure Analysis

Reflection data were collected by a R-AXIS RAPID-F diffractometer from Rigaku. Structure was solved by direct methods (SHELXS-86) and refinement was carried out by the least squares method in teXsan program package.

3. Polarized Reflection Spectra

Polarized reflection spectra in the visible region were measured on single crystals by means of a microscope-spectrophotometer (UMSP 80 from Carl Zeiss) equipped with an R928 photomultiplier (HTV). Reflectivities were corrected relative to the reflection standard of silicon carbide.

Results and Discussion

1 Crystallographic Parameters and Molecular Conformation of DPPP

Table 1 details the crystallographic parameters for DPPP I together with those of DPPP II. In DPPP I, the crystal system is monoclinic and the space group is $P2_1/n$. These are two molecules in the unit cell. On the other hand, the space group and molecular symmetry of DPPP II are $P2_1/c$ and C_1 , respectively. There are 4 molecules at the general positions in the unit cell.

Figures 4(a) and 4(b) show the ORTEP plots of DPPP I and DPPP II, respectively. Because of the C_i symmetry in DPPP I, the pyridyl rings are twisted in the same direction by about 6.5° with respect to the heterocyclic ring. In DPPP II, the two pyridyl rings are asymmetrically twisted in opposite directions by 4.2° and 15.3° .

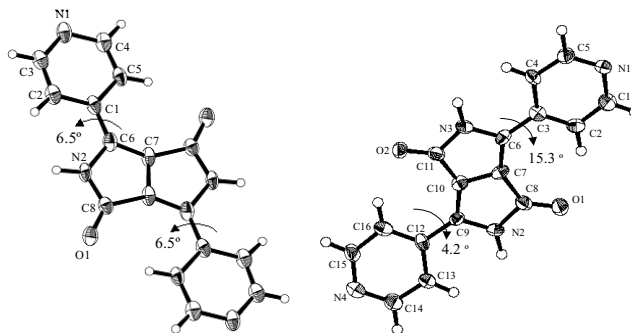


Figure 4. ORTEP plots: (a) DPPP I and (b) DPPP II.

2. Molecular Arrangement and Intermolecular Hydrogen Bonds

Figures 5(a) and 5(b) shows the projection of the crystal structure of DPPP I onto the (b,c) and (a,c) planes, respectively. The dotted lines represent the intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring one (N/O distance: 2.85\AA). There are chains of $\text{NH}\cdots\text{O}$ H-bonds along the b -axis. This type of two-dimensional H-bond network is found in common in all DPP pigments. The molecules are arranged in a zigzag fashion along the c -axis and stacked along the a -axis. It is also to be noted that two N atoms in each pyridyl ring remain free and can accept protons. For this reason, DPPP I is ideal for applications of acid and H_2 gas sensors.

Table 1. Crystallographic Parameters of DPPPs I and II.

	DPPP I	DPPP II
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
Molecular symmetry	C_i	C_1
Z	2	4
a (\AA)	3.722(1)	3.695(1)
b (\AA)	6.263(3)	18.201(2)
c (\AA)	26.506(9)	18.456(2)
β ($^\circ$)	94.41(2)	94.68(1)
V (\AA^3)	616.0(4)	1237.1(3)

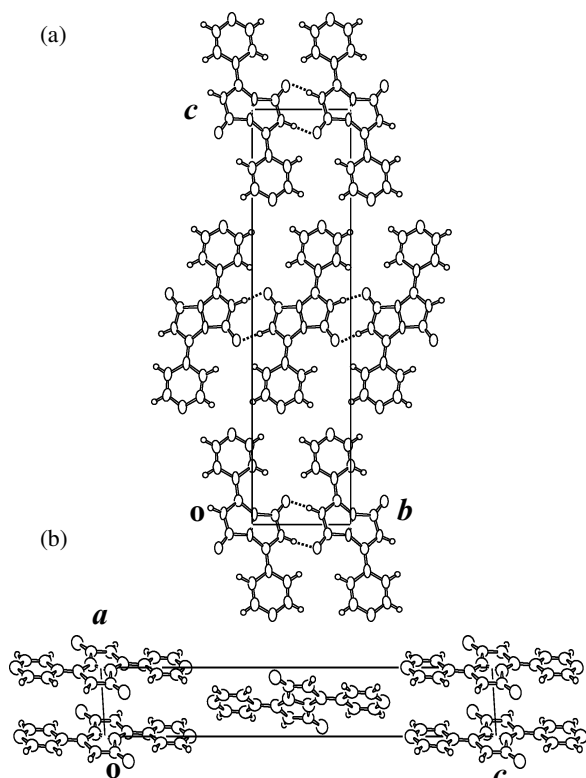


Figure 5. Projection of DPPP I onto: (a) (b,c) and (b) (a,c) plane.

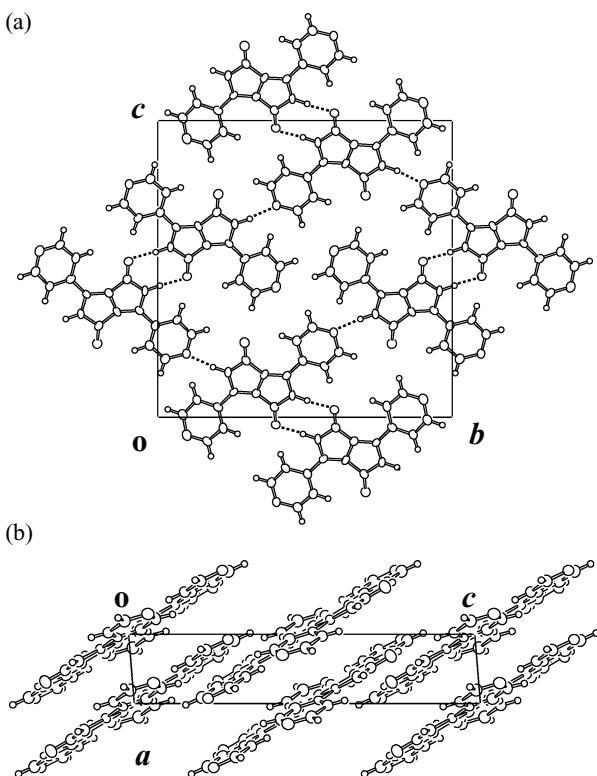


Figure 6. Projection of DPPP II onto: (a) (b,c) and (b) (a,c) plane.

On the other hand, the H-bond fashion and H-bond network are quite different in DPPP II. The projection of the crystal structure onto the (b,c) and (a,c) planes is shown in Figs. 6(a) and 6(b), respectively. On the (b,c) plane, there are two types of the H-bond. One is the $\text{NH}\cdots\text{O}$ between the

NH group of one molecule and the O atom of the neighboring one (N/O distance: 2.84 \AA). The other is based on the $\text{NH}\cdots\text{N}$ between the NH group of one molecule and the N atom of the pyridyl ring of the neighboring molecule (N/N distance: 2.89 \AA). In each molecule, there are two H-bonds of the $\text{NH}\cdots\text{O}$ type as well as two bonds of the $\text{NH}\cdots\text{N}$ type. In addition, there remains one free N atom. The molecule-pairs bonded by two mutually-faced $\text{NH}\cdots\text{O}$ hydrogen bonds behave as the repeating unit in the crystal lattice and are arranged in a zigzag fashion along the b -axis as well as the c -axis on the molecular plane. There is also a $\text{NH}\cdots\text{N}$ and two bifurcated $\text{NH}\cdots\text{O}$ bonds. The present two-dimensional H-bond network is quite unique of DPPP II, not found in other DPPs. The molecules are stacked along the a -axis. In DPPP II, one N atom is hydrogen-bonded while the other remains free. Therefore DPPP II is less sensitive to protons. For this reason, DPPP II is appropriate for colorant applications.

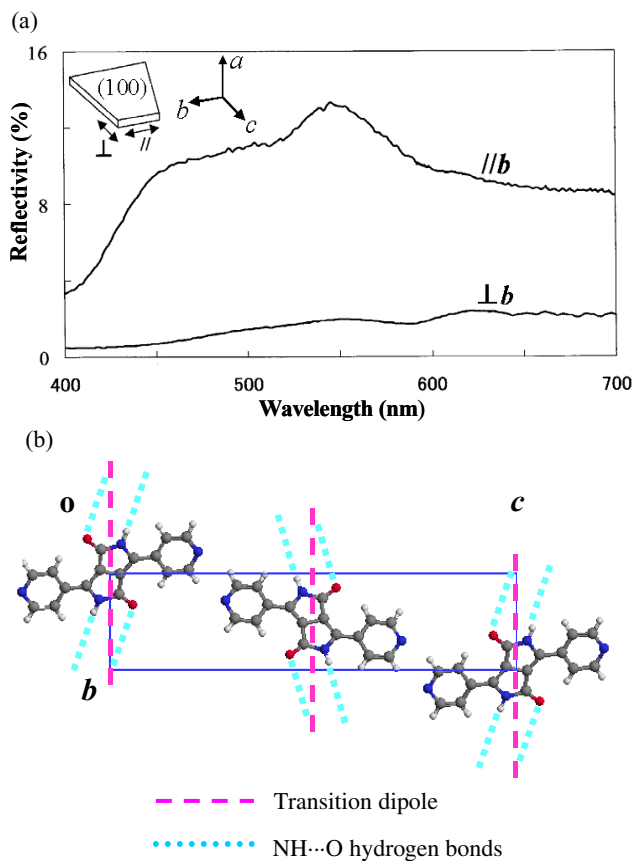
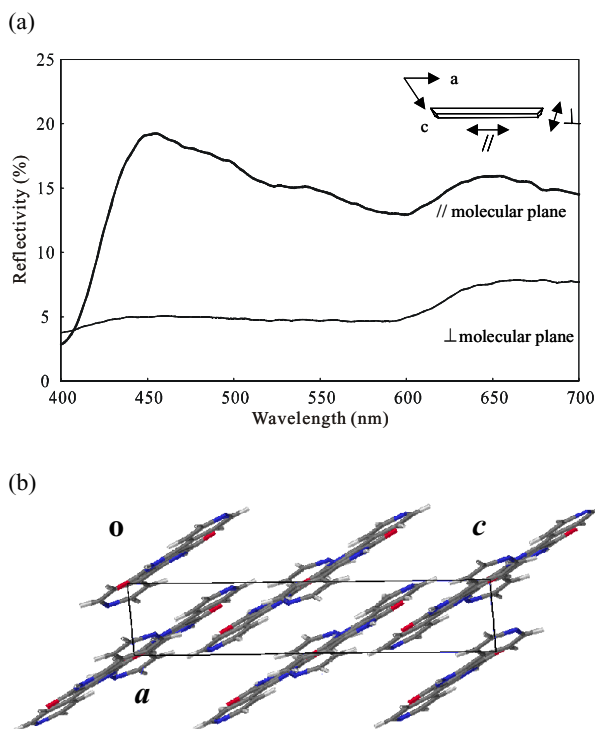


Figure 7. (a) Polarized reflection spectra of DPPP I measured on the (100) plane of single crystals and (b) projection of DPPP I onto the (b,c) plane.

3. Polarized Reflection Spectra Measured on Single Crystals

Figures 7(a) and 7(b) show the polarized reflection spectra measured on the (*b,c*) plane of DPPP I single crystals and the corresponding. Polarized light was introduced in parallel and perpendicular to the *b*-axis. A prominent reflection band appears around 550 nm together with a reflection shoulder around 450 nm for polarization parallel to *b*-axis. On the other hand, these intense reflection bands completely disappear for polarization perpendicular to the *b*-axis. This indicates that the transition dipole points along the *b*-axis; the direction of the NH \cdots O intermolecular H-bonds.

Figures 8(a) and 8(b) show the polarized reflection spectra of DPPP II measured on the (*a,c*) plane of single crystals together with its corresponding projection, respectively. (The rise of reflection around 600 nm and subsequent constant reflection is due to the reflection from the rear crystal.)



Figures 8 (a) Polarized reflection spectra of DPPP II measured on the (*a,c*) plane of single crystals and (b) projection of DPPP II onto the (*a,c*) plane.

Conclusion

The crystal structure of DPPP I has been determined and compared with that of previously reported DPPP II. The conclusions drawn from the present investigation can be summarized as follows.

1. DPPP I is found to crystallize in the space group of $P2_1/c$ with $Z=4$.
2. There are four NH \cdots O hydrogen bonds per molecule in DPPP I. The N atoms of the two pyridyl rings are free to accept protons. Therefore, DPPP I is ideal for applications of acid and H $_2$ gas sensors.
3. The transition dipole of DPPP I points along the direction of the NH \cdots O hydrogen bond.
4. In DPPP II, there are two types of H-bonds: NH \cdots O as found in all DPP pigments and NH \cdots N between the NH group of one molecule and the N atom of the pyridyl ring of the neighboring molecule. One of the two N atoms of the pyridyl rings is protected by NH \cdots N hydrogen bond. Therefore, DPPP II is appropriate for colorant applications.

Reference

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Biography

Imoda Tomohiko received his Bachelor of Engineering from Yokohama National University in 2004. He is currently in the graduate course for physics at Yokohama National University. His research interest includes crystal and electronic structure of organic pigments together with their application.