

Polymorph of 1,4-diketo-3,6-bis-(4'-dipyridyl)-pyrrolo-[3,4-*c*] pyrrole and their hydrogen bond network: A material for H₂ gas sensor

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Abstract

Diketodiphenylpyrrolopyrroles (DPP) are industrially important red pigments. The title compound (DPPP) is a dipyrindyl derivative that possesses a high proton affinity because of the N atoms of the pyridyl ring. A drastic change in shade as well as electrical conductivities by several orders of magnitude is observed due to protonation at the N-atom. Therefore, DPPP has newly attracted attention as a material for H₂ gas sensors. Then, we noticed that there are two crystal phases: one is quite sensitive to protons (phase I grown from the vapor phase) while the other is rather resistant to protonation (phase II recrystallized from solution). Therefore, structure analysis has been carried out in the present investigation in order to clarify the correlation between the structure and proton affinity. A striking difference is recognized in intermolecular hydrogen bonds between two phases: phase I is characterized only by NH...O hydrogen bonds where two N atoms of the pyridyl rings remain free. On the other hand, phase II includes two types of the H-bond based on NH...O and NH...N where the one N atom of the pyridyl ring is used by NH...N hydrogen bond and the other remains unused (i.e. free). Therefore, phase I is found to correspond to the phase which exhibits a high proton affinity while phase II is the one which is rather inactive for protons.

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1. Introduction

Diketodiphenylpyrrolopyrroles (for example DPP: Fig. 1(a)) are industrially important organic pigments used not only for paint industries as well as in the imaging areas [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

a dipyrindyl derivative that shows a high proton affinity because of the N atom of the pyridyl ring [2]. Protonation at the N atom (shown in the inset of Fig. 2) brings about a drastic color change from vivid red to violet, accompanied by changes in electrical conductivity and photoconduction [2]. For example, the absorption maximum is displaced from 540 to 580 nm due to protonation by vapor of nitric acid as shown in Fig. 2 while the electrical resistivity reduces by several orders of magnitude. The proton affinity is obviously a negative factor for colorants because the color change easily occurs in pigment-dispersed layers due to gradual liberation of protons from the polymer matrix. The proton affinity is, however, a positive factor for applications for H₂ gas sensors. For this reason, we have initiated the investigation for H₂ gas sensors [3].

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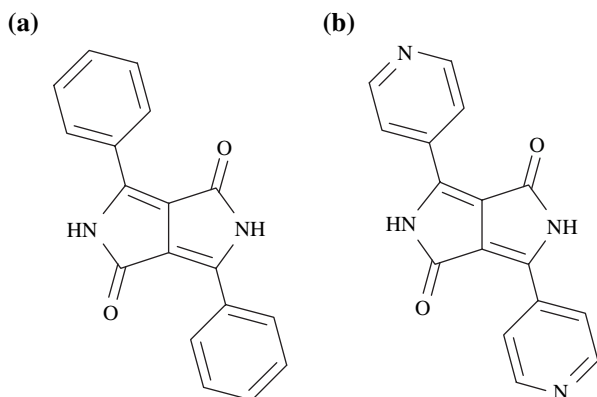


Fig. 1. Molecular conformation of: (a) DPP and (b) DPPP.

Then, we found that there exist two crystal phases in the solid state of DPPP: one is quite sensitive to protons (phase I: grown from the vapor phase) while the other exhibits a poor proton affinity (phase II: recrystallized from solution). We have successfully isolated these single crystals and analyzed the crystal structure of phases I and II in order to elucidate the correlation between the structure and proton affinity.

The present paper deals with the crystal and electronic structure of phases I and II of DPPP with special attention to their hydrogen bond network.

2. Experiment

2.1. Sample preparation and crystal growth

DPPP was synthesized according to the method described in Ref. [4] and purified six times by sublimation, using a two-zone furnace [5]. Single crystals of phase I were grown from the vapor phase in a closed system based on a two-zone furnace. On the other hand, single crystals of phase II were grown by recrystallization from solution in *N,N*-dimethylacetamide using an autoclave (Taiatsu Co. Ltd.; model TPR-2).

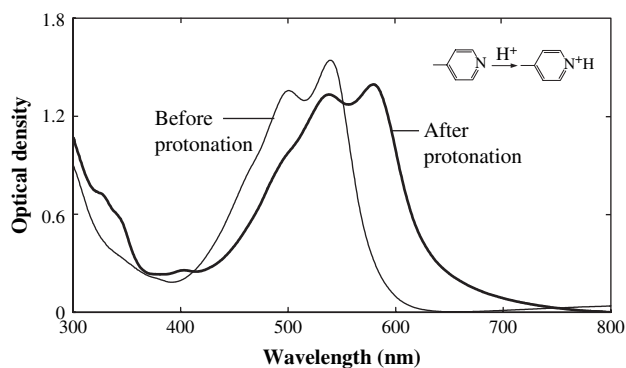


Fig. 2. Solid-state spectra of evaporated DPPP before and after protonation with the vapor of nitric acid.

2.2. Structure analysis

Reflection data were collected by an 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.

2.3. 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.

3. Results and discussion

3.1. Crystallographic parameters and molecular conformation of DPPP

Table 1 details the crystallographic parameters for phase I together with those of phase II [6]. In phase 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 phase II are $P2_1/c$ and C_1 , respectively. There are four molecules at the general positions in the unit cell.

Fig. 3(a) and (b) show the ORTEP plots of phases I and II, respectively. Because of the C_i symmetry in phase I, the pyridyl rings are twisted in the same direction by about 6.5° with respect to the heterocyclic ring. In phase II, the two pyridyl rings are asymmetrically twisted in opposite directions by 4.2° and 15.3° .

3.2. Molecular arrangement and intermolecular hydrogen bonds

Fig. 4(a) and (b) shows the projection of the crystal structure of phase I onto the (b,c) and (a,c) planes, respectively. The dotted lines represent the intermolecular hydrogen bonds between the NH group of one

Table 1
Crystallographic parameters for phases I and II of DPPP

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

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