

# Electronic Characterization of 1-Keto-4-thioketo-3,6-diphenylpyrrolo[3,4-c]pyrrole

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## Abstract

Electronic characterization of mono-keto-mono-thioketo-pyrrolopyrrole (MTPP) has been carried out in order to explore new electronic applications. The crystal structure of MTPP is found to be isomorphous with that of modification I of dithioketopyrrolopyrrole (DTPP). The color is nearly between those of diketopyrrolopyrrole (DPP) and DTPP. The intermolecular hydrogen bonds based on both  $\text{NH}\cdots\text{O}$  and  $\text{NH}\cdots\text{S}$  are found to be considerably weak as compared with those of DPP ( $\text{NH}\cdots\text{O}$ ) and DTPP ( $\text{NH}\cdots\text{S}$ ). The absorption spectrum of MTPP suggests a potential application for LCD blue-filters.

## Introduction

The title compound, 1-keto-4-thioketo-3,6-diphenylpyrrolo-[3,4-c]-pyrrole (MTPP) is a mono-thionated derivative of diketopyrrolopyrrole (DPP) known as a novel red pigment on the market.<sup>1)</sup> On the other hand, dithioketopyrrolopyrrole (blue pigment: DTPP) has also attracted attention as a material useful for photoreceptors for laser printers<sup>2)</sup> as well as optical disks<sup>3)</sup> based on GaAsAl laser diodes. Because of the hybrid structure between DPP and DTPP, MTPP has been synthesized in the expectation of the appearance of novel electronic properties and applications. In the present investigation, electronic characterization of MTPP has been carried out on the basis of the crystal structure and intermolecular interactions.

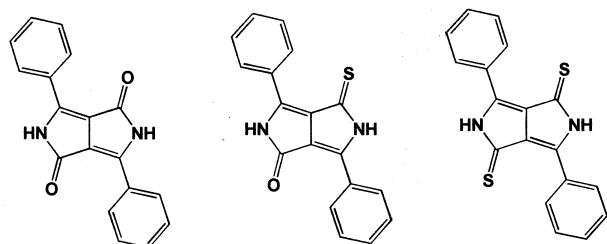


Figure 1 Molecular structures of DPP, MTPP and DTPP.

## Results and Discussion

### Crystal Structure

The crystal data of MTPP are<sup>4)</sup>:  $\text{C}_{18}\text{H}_{12}\text{N}_2\text{OS}$ ,  $M_r = 304.37$ , monoclinic,  $P2_1/n$ ,  $a=7.570(3)$ ,  $b=4.869(3)$ ,  $c=19.616(4)$  Å,  $\beta=99.07(3)^\circ$ ,  $V=714.0(6)$  Å<sup>3</sup>,  $Z=2$ ,  $D_s=1.416$ ,  $D_m=1.372$  Mg m<sup>-3</sup>. MTPP is found to be isomorphous with modification I of DTPP.

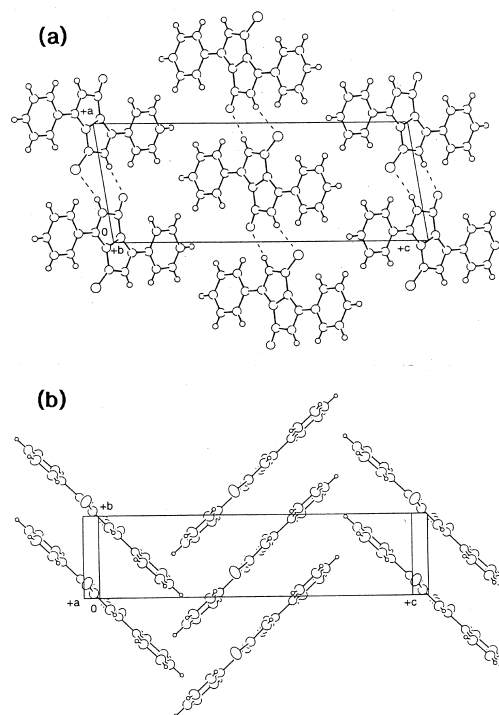


Figure 2 Projection of the structure onto the (a,c) plane.

Fig.2 shows the projection of the crystal structure onto the (a,c) plane, in which the intermolecular hydrogen bonds are designated by dotted lines. On each side of the molecule, two kinds of the hydrogen bonds are formed: one is based on  $\text{NH}\cdots\text{O}$  and the other is  $\text{NH}\cdots\text{S}$ . The molecules are stacked in a herringbone fashion along the b-axis.

### Solid-State Spectra of Evaporated MTPP

Fig. 3 shows the absorption spectra of evaporated MTPP before and after vapor treatment. The absorption bands as evaporated appear around 550 and 610 nm together with a shoulder at about 510 nm. Vapor treatment then brings about a small shoulder around 700 nm and it grows up finally to an intense band as shown in Fig.3, while the intensity of the two visible bands around 550 and 610 nm is greatly diminished.

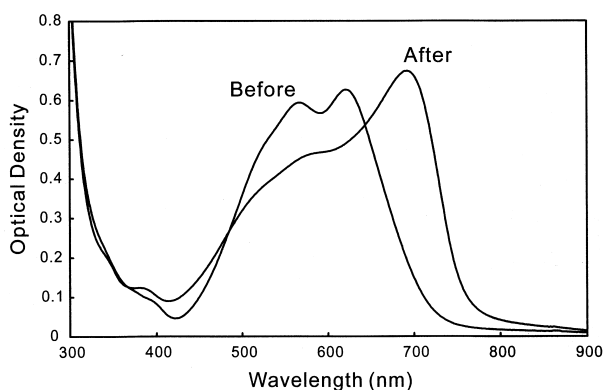


Figure 3 Absorption spectra of evaporated MTPP.

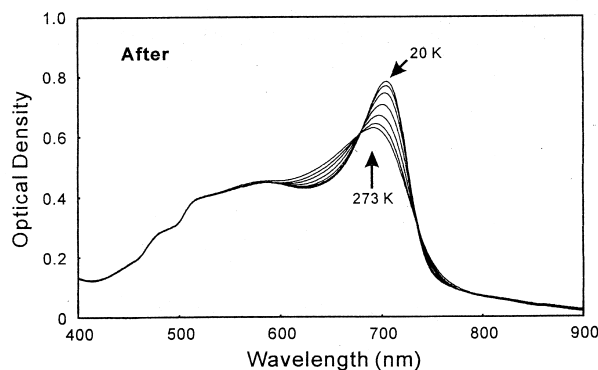
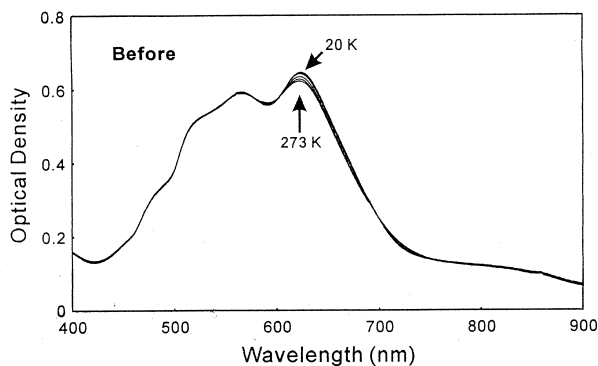


Figure 4 Temperature dependence of evaporated MTPP.

The temperature dependence of absorption spectra before and after vapor treatment were measured in the temperature range between 20 and 300 K (Fig.4). No

noticeable spectral change was observed in the absorption spectra before vapor treatment. On the other hand, the longest-wavelength band at 700 nm exhibits a remarkable temperature dependence, indicating that the present band is quite sensitive to lattice contraction at low temperatures and is due to intermolecular interactions.

### X-ray Diffraction Diagrams

Fig.5 shows the X-ray diffraction diagrams before and after vapor treatment. The diagram before vapor treatment is characterized by a single diffraction peak at about  $2\theta=6.5^\circ$ . Vapor treatment then induces crystallization as shown by the diffraction peaks at about  $13^\circ$ ,  $19^\circ$  and  $26^\circ$ . The diffraction peak around  $26^\circ$  corresponds to the diffraction along the stacking axis. This indicates that the molecules are ordered along the stacking axis due to vapor treatment and that the ordering of the molecules displaces the absorption band from 610 nm to 700 nm (Fig.3).

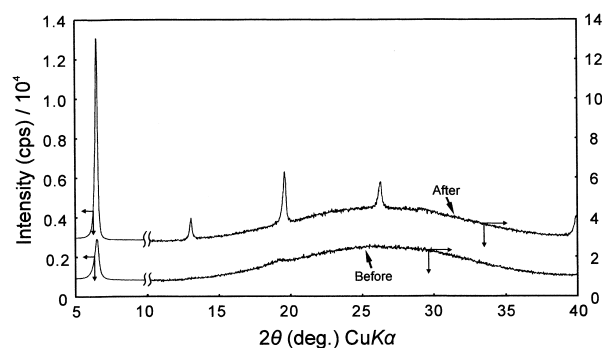


Figure 5 X-ray diffraction diagram of evaporated MTPP.

Trial was then made in vain to assign the observed diffraction peaks on the basis of the analyzed crystal structure. Particularly, the diffraction peak around  $6.5^\circ$  was not assignable. This indicates that the phases of evaporated MTPP as well as vapor-treated MTPP are different from the phase determined by the X-ray structure analysis.

### Polarized Reflection Spectra

Fig.6 shows the polarized reflection spectra measured on the (001) plane of MTPP single crystals. Prominent reflection bands appear around 550 and 620 nm for polarization parallel to the  $a$ -axis. Polarization perpendicular to the  $a$ -axis quenches these visible bands. Instead, a small reflection band is observed around 640 nm. The fact that the two visible bands (550 and 620 nm) appear and disappear simultaneously by polarized light indicates that the two bands belong to the same electronic transition and that the longest-wavelength band is attributed to the 0-0 transition, and the second-longest broad band might be composed of the 0-1 and 0-2 transitions. The small band around 640 nm, which appears with polarized light along the stacking axis, could be ascribed to an intermolecular charge transfer (CT) band.

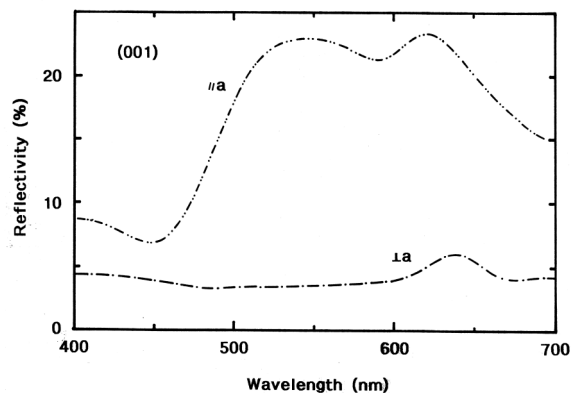


Figure 6 Polarized reflection spectra of MTPP single crystals.

### Direction of the Transition Moment and Exciton Coupling Effects

As apparent from the polarized reflection spectra (Fig.6), the transition moment of MTPP points the direction of the intermolecular hydrogen bonds based on  $\text{NH}\cdots\text{O}$  and  $\text{NH}\cdots\text{S}$ . On the one side, the intermolecular H-bonds hold MTPP molecules together to stabilize the system and also to suppress the solubility in solvents. On the other hand, the H-bonds align the transition moments in a fashion "head-to-tail" and thus displace greatly the absorption band towards longer wavelengths. This is the effect caused by interactions between transition dipoles ("exciton coupling effect"). The spectral displacements due to exciton coupling in DPP derivatives and DTPP are fully discussed in our previous reports.<sup>5,6)</sup>

### CT Transition Along the Stacking Axis

A small reflection band appears around 640 nm as a result of the excitation along the stacking axis (Fig.3). The present band can be assigned to an intermolecular CT transition. This sort of CT transition is often observed in sulfur-containing compounds, in which the molecules are stacked in a herringbone fashion. In fact, a small reflection band has also been observed along the stacking axis in modifications I and II of DTPP.<sup>6)</sup>

### Similarities Between MTPP and DTPP

The electronic properties of MTPP are more similar to DTPP than DPP. Among others, the crystal structure of MTPP is isomorphous with modification I of DTPP. In modifications I and II as well as in MTPP, there observed two intense reflection bands in the visible region when excited along the molecular plane; whereas a small CT reflection band along the stacking axis.

In DTPP, there are three crystal modifications I, II and III. Modifications I and II of DTPP are known to be transformed into modification III due to vapor treatment to give an intense near-IR absorption. The near-IR absorption alone exhibits a considerable temperature dependence and has been interpreted as arising from a molecular arrangement characterized by the "bricks in a brick wall" structure.<sup>6)</sup> This is the consequence of the exciton coupling

effects due to molecular arrangement of modification III. A similar behavior is also found in MTPP. Vapor treatment of MTPP brings about molecular re-arrangement (Fig.5), accompanied by a large spectral displacement from 610 to 700 nm (Fig.3). The band at 700 nm alone exhibits a significant temperature dependence (Fig.4). These observations suggest that the phase of the evaporated, vapor-treated MTPP corresponds to that of modification III in DTPP as characterized by the "bricks in a brick wall" structure.

### LCD Blue Filter

As shown in Fig.3, the optical absorption of MTPP is minimum around 420 nm and the visible bands cover the spectral region of green (555 nm) and red (620 nm). Therefore, MTPP can be used as a blue filter with a high purity for LCD applications. The spectral characteristic is equivalent to that of the conventional green filter based on copperphthalocyanine, or even exceeds its performance.

### Summary

The electronic properties of MTPP has been characterized on the basis of the crystal structure and intermolecular interactions. The present investigation can be summarized as follows:

1. The crystal structure of MTPP is isomorphous with that of DTPP I. Therefore, MTPP behaves spectroscopically as DTPP rather than DPP.
2. The polymorphic properties of DTPP are also observed in MTPP.
3. The absorption spectrum of MTPP suggests a potential application for LCD blue filters.

### References

1. A. Iqbal, L. Cassar, A. C. Rochat, J. Pfenninger and O. Wallquist: *J. Coat. Tech.* **60**, 37-45 (1988).
2. J. Mizuguchi and A. C. Rochat: *J. Imag. Sci.* **32**, 135-140 (1988).
3. J. Mizuguchi, G. Giller and E. Baeriswyl: *J. Appl. Phys.* **75**, 514-518 (1994).
4. J. Mizuguchi: *Z. Krist.* **214**, 677-680 (1999).
5. J. Mizuguchi: *J. Phys. Chem. A*, **104**, 1817-1821 (2000).
6. J. Mizuguchi: *Denshi Shashin*, **37**, 58-66 (1998).

### 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 from the University of Bern in 1994. He worked in the field of organic semiconductors 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.