Local Similarity Between Mixed Crystals of Two Components and Crystals of Their Hybrid Single Component in Pyrrolopyrrole Compounds

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Abstract

Diketopyrrolopyrroles are typical hydrogen-bonded pigments of red color based on the skeleton of 1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP). Our previous investigation revealed that the 1:1 mixed crystal (MX-DPP) composed of DPP and its (*t*-butylphenyl) derivative (BTB-DPP) gives practically the same electronic spectra as well as X-ray diffraction diagram as those of the hybrid compound of DPP and BTB-DPP (MTB-DPP). In order to elucidate the present coincidence, electronic structure has been investigated on single crystals of MX-DPP and MTB-DPP on the basis of the structure analysis. The space groups of both crystals are found to be the same (*P*-1) and the crystallographic parameters are quite similar. In both MX-DPP and MTB-DPP, the same molecular environment (in other words, the "local similarity") is achieved throughout the crystal. Furthermore, the polarized reflection spectra measured on single crystals also gave approximately the same results. These experimental facts led us to conclude that the "local similarity" plays the key role in the determination of the crystal and electronic structures in MX-DPP and MTB-DPP.

Introduction

Diketopyrropyrrole (abbreviated to DPP; Figure 1) pigments are industrially important red pigments based on the novel diketopyrrolopyrrole chromophore.[1] DPPs are also used as colorants for imaging areas as well as color filters for LCD applications.

Figure 1 shows three kinds of DPP derivatives: DPP,[2] BTB-DPP,[3] and MTB-DPP.[4] Both DPP and BTB-DPP are symmetrical molecules; whereas MTB-DPP is an asymmetrical molecule characterized by a hybrid structure between DPP and BTB-DPP. In our previous investigation, DPP and BTB-DPP are found to form a 1:1 mixed crystal (MX-DPP) whose spectroscopic and crystallographic behavior is surprisingly similar.[5] The present phenomenon is scientifically of great interest why two symmetrical molecules give the same optical and structural properties as those of asymmetrical one. At the same time, this outstanding effect also makes sense from a practical point, because the mixed crystal based on two kinds of inexpensive, symmetrical molecules gives the same color as that of expensive, asymmetric molecules. For these reasons, an attempt was made in the present investigation to clarify the electronic structure MX-DPP and MTB-DPP in both evaporated films and single crystals. Special attention was paid to the crystal growth of single crystals and their subsequent structure analysis.

This paper describes the spectroscopic and structural results of MX-DPP and MTB-DPP and discusses their properties together with simulated crystal structures proposed by Karfunkel, Mizuguchi and others.[6]

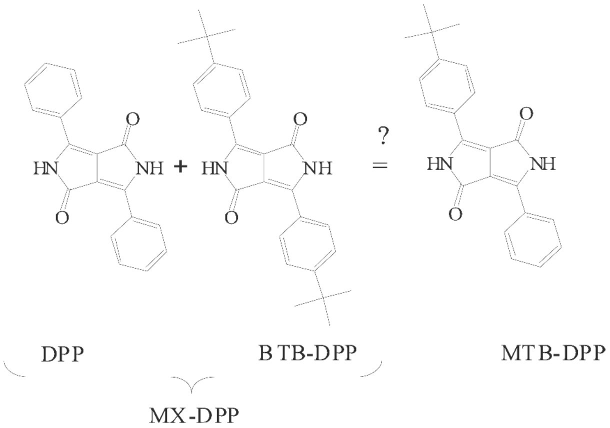


Figure 1. Schematic diagram for MX-DPP and MTB-DPP.

Experiment

DPP and BTB-DPP were obtained from Ciba Specialty Chemicals. MTB-DPP was synthesized according to the method described in ref.5. DPP, BTB-DPP and MTB-DPP were purified once by sublimation, using a two-zone furnace.[7] The MX-DPP powders were prepared from DPP and BTB-DPP by deprotonation with sodium hydroxide, followed by protonation with hydrochloric acid.

Evaporated thin films of MX-DPP and MTB-DPP were prepared onto glass substrates using conventional vacuum evaporation equipment. Plain glass slides were used as substrate for measurements for the visible absorption spectra and X-ray diffraction diagrams, respectively.

The single crystals of MX-DPP and MTB-DPP were grown from the vapor phase in a closed system, using a two-zone furnace. In MX-DPP, we have obtained a number of tiny single crystals of the typical dimension of about $200 \times 100 \times 10\ \mu m^3$. The crystal parameters were successfully determined, but the crystal was too small to carry out its full structure analysis. In MTB-DPP, a number of platelet-like crystals were obtained and the structure was successfully solved.[4]

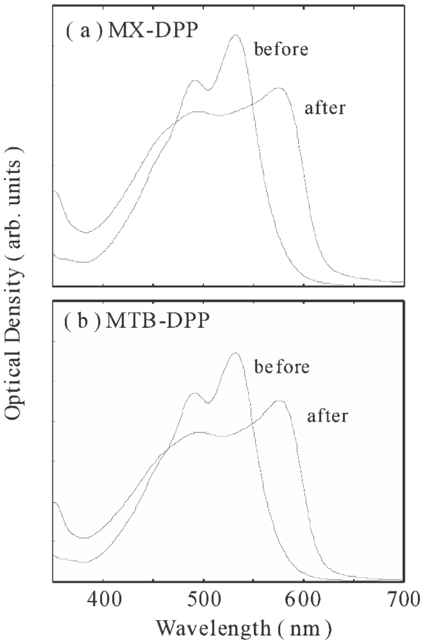
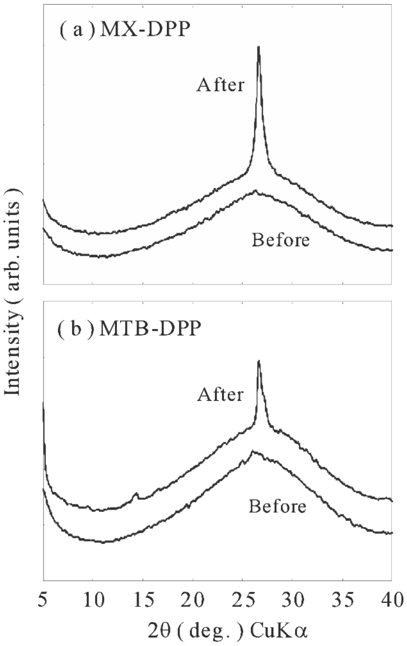


Figure 2. Solid-state spectra in evaporated films for MX-DPP and MTB-DPP.

Results and Discussion

1. Solid-State Spectra and X-Ray Diffraction Diagrams in Evaporated Films

Figures 2 (a) and (b) show the solid-state spectra of evaporated films for MX-DPP and MTB-DPP before and after vapor treatment, respectively. It is remarkable to note that the absorption spectra in both samples before and after vapor treatment are remarkably similar to each other. The absorption spectra before vapor treatment are typical of DPP derivatives peaking at about 540 nm. However, the longest-wavelength band is then displaced toward longer wavelengths around 576 nm when the evaporated films are exposed to acetone vapor for about 15 hours. Then, the color changes from vivid red to bluish red and the resulting spectral shape is quite unusual as compared with that of ordinary pyrrolopyrroles.



Figures 3. X-ray diffraction diagrams in evaporated films for MX-DPP and MTB-DPP.

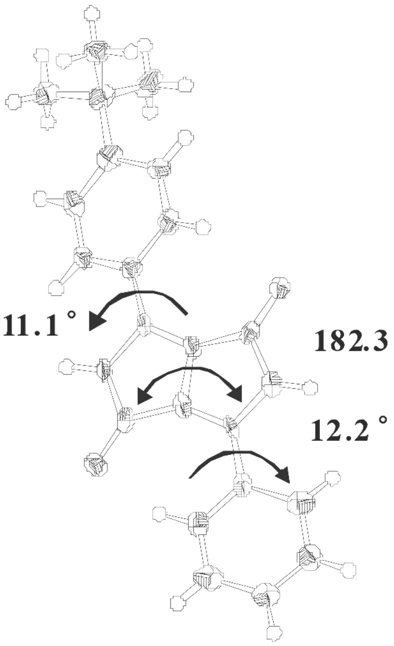


Figure 4. Molecular conformation for MTB-DPP.

Figures 3 (a) and (b) show the X-ray diffraction diagrams for evaporated MX-DPP and MTB-DPP before and after vapor treatment, respectively. The broad diffraction band around 26° is due to the glass substrate used. No noticeable diffraction peaks are recognized in both samples before vapor treatment, suggesting that the phase is rather amorphous. However, in this state, the two-dimensional network of intermolecular hydrogen bonds is formed on the entire molecular plane in both samples as shown by IR spectra. The present crystallization in both samples as shown by the diffraction peak around 26° hydrogen bonds are based on the NH group of one molecule and the O atom of the neighboring one (NH stretching around 3100 cm^{-1} and C=O stretching around 1640 cm^{-1}). Vapor treatment then brings about crystallization in both samples as shown by the diffraction peak around 26° (interplanar distance: about 3.5 Å). This indicates that the molecules are ordered along the stacking axis due to vapor treatment. In this way, the molecules are fully stabilized not only on the molecular plane but also along the stacking axis.

2. X-ray Structure Analysis

Table 1 details the crystallographic parameters for MX-DPP and MTB-DPP together with those of simulated ones. The space groups of both crystals are found to be the same (*P*-1) and the crystallographic parameters are quite similar.

An ORTEP plot is shown in Figure 4 for MTB-DPP.[4] The phenyl rings are twisted asymmetrically by about 12.2° and 11.1° in opposite directions with respect to the heterocyclic ring system. The heterocyclic ring system is not entirely planar, but is folded in the middle with a dihedral angle of about 177.7°.

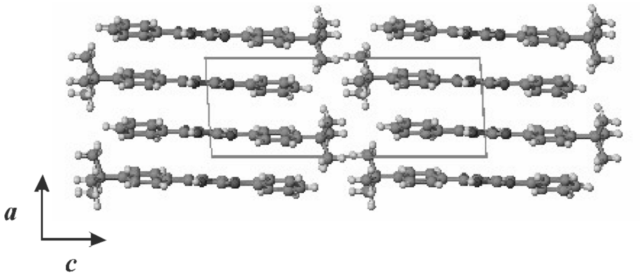


Figure 5. Projection onto the (a,c) plane in MTB-DPP.

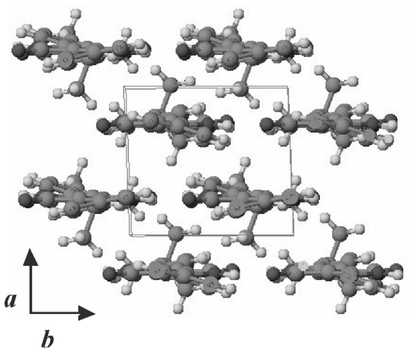


Figure 6. Projection onto the (a,b) plane in MTB-DPP.

Figure 5 shows the projection of the crystal structure onto the (*a,c*) plane in MTB-DPP. The molecules are stacked alternately along the *a*-axis. In each lattice plane, the *t*-butyl group of one molecule faces the phenyl ring of the neighboring one. Figure 6 shows the projection onto the (*a,b*) plane. The molecules are stacked in a fashion “bricks in a brick wall”. Along the *b*-axis, there are chains of intermolecular hydrogen bond between the NH group of one molecule and the O atom of the neighboring molecule.

3. Comparison of the Crystal Structures of MX-DPP and MTB-DPP with Those of Simulated Ones

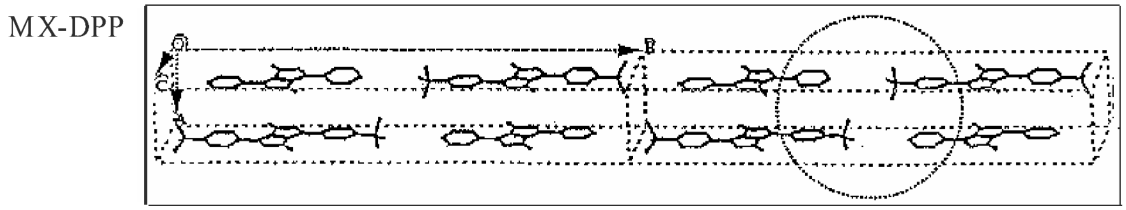
As shown in Table 1, the space group experimentally obtained for MX-DPP and MTB-DPP agrees with that of simulated one (*P*-1). In addition, the lattice parameter are also quite similar to each other, although the *c* lattice of the simulated MX-DPP is twice as that of the experimental one.

Figure 7 shows the molecular arrangement of simulated MX-DPP and MTB-DPP. In each lattice plane, the *t*-butyl group of one molecule faces the phenyl ring of the neighboring one in both compounds. The area surrounded by dotted circles is called “local similarity” which prevails throughout the both crystals. In addition, the molecular arrangement of experimentally obtained MTB-DPP is in good agreement with that of the simulated one. This suggests that the simulated molecular arrangement for MX-DPP might also be the case in MX-DPP.

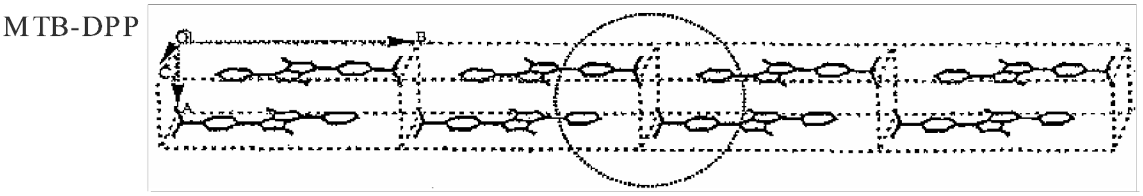
4. Polarized Reflection Spectra

Figures 8 (a) and (b) show the polarized reflection spectra measured on single crystals of MX-DPP and MTB-DPP by means of a microscope-spectrophotometer. In MX-DPP, polarized light was introduced parallel or perpendicular to the long-crystal axis. A prominent reflection band appears around 600 nm together with a reflection shoulder around 480 nm for polarization parallel to the long-crystal axis. On the other hand, the reflection bands are completely quenched for polarization perpendicular to the long-crystal axis.

In MTB-DPP, reflection measurements were made on the (*a,b*) plane whose projection is shown in Figure 6. The strong bands appear and disappear for polarization parallel and perpendicular to the *b*-axis, respectively. This result evidently indicates that the transition dipole of MTB-DPP points along the *b*-axis, *i.e.* the direction of the intermolecular hydrogen bonds. That is, the hydrogen bonds align the transition dipole of the molecule in the solid state in a way “head-to-tail” and this causes a large bathochromic shift to occur on going from solution to the solid state. Since the reflection spectra for both MX-DPP and MTB-DPP are so similar, the “local similarity” is presumably the determinant factor for the coincidence of the reflection spectra as well as of the X-ray diffraction characteristics.



Simulation: (P-1): $a, b, c, \alpha, \beta, \gamma$ = 6.7, 7.3, 37.0, 95.8, 90.0, 89.5
Experiment: (P-1): a, $b, c, \alpha, \beta, \gamma$ = 6.65, 7.38, 18.46, 82.5, 83.7, 88.2



Simulation: (P-1): $a, b, c, \alpha, \beta, \gamma$ = 6.7, 7.3, 18.5, 95.0, 89.1, 89.1
Experiment: (P-1): a, $b, c, \alpha, \beta, \gamma$ = 6.45, 7.09, 17.95, 84.9, 86.1, 87.4

Figure 7. Molecular arrangement of simulated MX-DPP and MTB-DPP.[6]

Table. 1. Crystallographic parameters for MX-DPP and MTB-DPP.

	MX-DPP		MTB-DPP	
	Experimental	Simulated[6]*	Experimental[4]	Simulated[6]*
Molecular formula	$C_{18}H_{12}N_2O_2 + C_{26}H_{28}N_2O_2$	$C_{18}H_{12}N_2O_2 + C_{26}H_{28}N_2O_2$	$C_{22}H_{20}N_2O_2$	$C_{22}H_{20}N_2O_2$
Crystal system	triclinic	triclinic	triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1
Z	2	4	2	2
Molecular weight	688.81	688.81	344.41	344.41
Molecular symmetry	—	—	C_1	—
a (Å)	6.65	6.7	6.45(2)	6.7
b (Å)	7.38	7.3	7.09(4)	7.3
c (Å)	18.46	37.0	17.95(6)	18.5
α(°)	82.5	95.8	84.9(4)	95.0
β(°)	83.7	90.0	86.1(1)	89.1
γ(°)	88.2	89.5	87.4(4)	89.1
Volume (Å^3)	891	1809.7	815.0(6)	901.4

*The cell has been transformed in accordance with the standard setting.

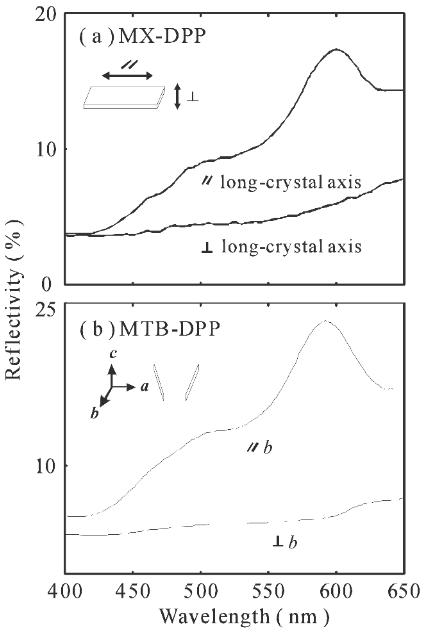


Figure 8. Polarized reflection spectra measured on single crystals for MX-DPP and MTB-DPP.

Conclusions

We have investigated the crystal and electronic structures of MX-DPP and MTB-DPP in evaporated films as well as in single crystals. The conclusions of the present investigation can be summarized as follows.

1. MX-DPP and MTB-DPP exhibit surprisingly similar spectroscopic and crystallographic characteristics in evaporated films and single crystals.
2. In MX-DPP and MTB-DPP, the “local similarity” is presumably achieved throughout the crystal so that the crystal and electronic structures are so similar between both compounds.

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Biography

Hirofumi Shikamori received his Bachelor of Education from Yokohama National University in 2001. He is currently in the graduate course for materials science at Yokohama National University. His research interest includes electronic characterization of organic pigments together with their electronic applications.