Molecular Distortion and Exciton Coupling Effects in β Metal-Free Phthalocyanine

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As pointed out in titanylphthalocyanine, molecular distortion (reduction in molecular symmetry) upon crystallization exerts a significant influence on the optical absorption in the near-IR region. The electronic spectra of β metal-free phthalocyanine (MfPc) has been investigated from the standpoint of molecular distortion and exciton coupling effects. Close examination of the crystal structure of MfPc revealed that the molecular symmetry is reduced from D_{2h} to C_i on going from solution to the solid state. Molecular distortion is found to enhance the band splitting in such a way that the longer-wavelength band is more displaced toward longer wavelengths while the shorter-wavelength band is more shifted toward shorter wavelengths. The electronic spectra of MfPc can mostly be interpreted in terms of the distortion of molecular framework. However, some exciton coupling effect is also observed, as shown by polarized reflection spectra on single crystals as well as the temperature dependence of absorption spectra.

1. Introduction

Metal-free phthalocyanine (MfPc shown in the inset of Figure 1) is a commercial blue pigment used widely for paint and automobile industries.[1,2] The first singlet−singlet transition called Q-band is responsible for the coloration in the visible region. Besides its use as a pigment, MfPc has also attracted attention as a photoconductor for laser printers based on GaAsAl laser diodes.[3] Several crystal modifications such as α, β, *x*, *etc.* are known to exist in X-ray powder diffraction diagrams.[1]

In the course of our studies on the mechanism of the near-IR absorption of titanylphthalocyanine (TiOPc), we found that the molecules are heavily deformed on going from solution to the solid state and that the molecular distortion (reduction in symmetry) exerts a profound influence on the optical absorption.[4] An in-depth investigation on the correlation between molecular distortion and optical absorption on the basis of molecular and crystal structures revealed that the band splitting sensitively occurs because the excited state of phthalocyanine compounds is doubly degenerate and this can easily be removed by a perturbation such as molecular distortion.[4] In fact, the band splitting becomes larger with molecular distortion. In this way, we have successfully interpreted the near-IR absorption of TiOPc as arising from the longer-wavelength band of the split bands.

The above investigation pointed out the importance of molecular distortion in the electronic transition of phthalocyanine compounds, while no investigation has been carried out from the viewpoint of molecular distortion. Our model is in marked contrast to the previous interpretations based on the exciton coupling effect called the Davydov splitting (factor group splitting).[5−7] An attempt was therefore made to characterize the electronic spectra of representative phthalocyanines in terms of the distortion of molecular framework.

The present paper discusses the electronic structure of MfPc from the standpoint of molecular distortion and exciton coupling effects. Attention is also focused on the separation of the effect between molecular distortion and exciton coupling.

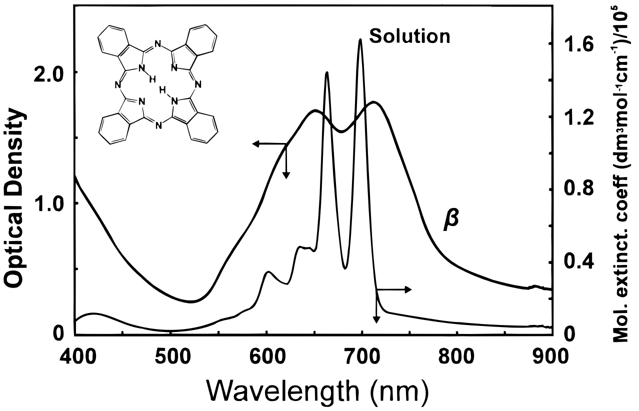

Figure 1. Solution spectrum in Cl-naphthalene and solid-state spectrum in an evaporated film of MfPc (film thickness: *ca.* 1000 Å).

2. Results and Discussion

2.1. Solution and Solid-State Spectra. The solution spectrum of MfPc in chloronaphthalene is shown in Figure 1 together with the solid-state spectrum for β phase in evaporated films. Both spectra give two absorption bands in the visible region due to D_{2h} symmetry.

2.2. Crystal Growth and Structure Analysis. The structure analysis for β-MfPc had already been done by Robertson[8] in 1936. His analysis was perfect with an experimental setup at that time but was not precise enough for the examination of molecular distortion because of the high standard deviation. So the structure was redetermined as described below.[9]

MfPc was purchased from Fluka Chemicals and purified four times by sublimation. The single crystals were then grown from the vapor phase, using a two-zone furnace.[10] A number of lustrous dark blue prisms were obtained after 24 h of vapor growth.

The reflection data were collected by a RigakuAFC7R diffractometer, and the structure was solved by direct methods, using SIR92.[11] Crystal data:[9] monoclinic, $C_{32}H_{18}$,N_8, M_r = 514.55, $P2_1/a$, $a = 19.870(7)$, $b = 4.731(7)$, $c = 14.813(7)$ Å,

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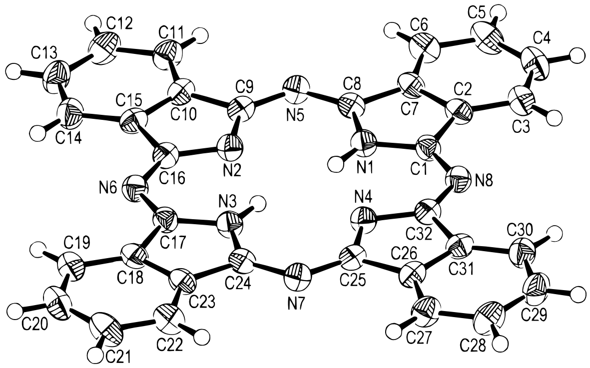


Figure 2. ORTEP diagram of β-MfPc.

TABLE 1: Molecular Distortion of MfPc in β-Phase Crystal and Optimized Geometry

		dihedral (deg.)	
plane 1	plane 2	X-ray (β-phase)	opt geo (solution)
N1,N2,N3,N4	phenyl C2...C7	1.86	0
N1,N2,N3,N4	phenyl C10...C15	2.32	0
N1,N2,N3,N4	phenyl C18...C23	−1.86	0
N1,N2,N3,N4	phenyl C26...C31	−2.32	0
Molecular symmetry		C_i	D_{2h}

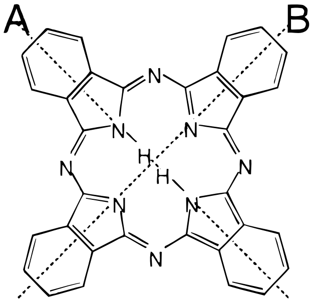
$\beta = 121.98(4)°$, $Z = 2$. The crystal structure is basically in good agreement with β-phase of MfPc reported by Robertson.[8] The ORTEP diagram is shown in Figure 2.

2.3. Molecular Distortion and Its Influence on the Optical Absorption Spectra. In order to quantify the extent of molecular distortion, we measured the angles between the plane of the four central nitrogen atoms (N1, N2, N3, and N4: plane 1) and the plane of each phenyl ring (plane 2). If all these angles are equal to zero, this is taken as D_{2h} symmetry. The angles are listed in Table 1 together with those of the optimized geometry (MNDO Hamiltonian in MOPAC93[12]) which corresponds to the conformation in solution. It is apparent that the molecule in the β-phase is slightly distorted and possesses the C_i symmetry, whereas the optimized structure is entirely planar and is characterized by D_{2h} symmetry.

The influence of the present molecular distortion is best evaluated by molecular orbital (MO) spectroscopic calculations using the x, y, z coordinate sets of the X-ray structure.[9] The bands calculated by the INDO/S Hamiltonian[13] are given in Table 2 together with the experimental values observed for solution and evaporated films. The transition moments A and B as well as their direction are set out in the inset. The effect of molecular distortion is clearly recognized in the calculation for the β-phase (C_i: 690.3/744.5 nm) as compared with that in solution (D_{2h}: 630.8/646.6 nm). The band splitting as given by the difference in energy between transitions A and B is about 1055 cm^{-1} in the β-phase, and this is much larger than the value of 387 cm^{-1} in solution. The difference of 668 cm^{-1} is therefore attributed to the effect of molecular distortion. This tendency is qualitatively in good agreement with experiment, as shown in Figure 1 and Table 2, indicating that the band splitting is larger in the solid state (1304 cm^{-1}) than in solution (744 cm^{-1}).

2.4. Polarized Reflection Spectra. In order to study the effect of exciton coupling on the absorption band, polarized reflection spectra shown in Figure 3 were measured on the (001) plane of a single crystal by means of a microscope spectrophotometer (UMSP80; Carl Zeiss) (Figure 3). A prominent reflection band appears around 730 nm for polarization perpendicular to the b-axis, accompanied by another dispersion peaking at 650 nm. An intense reflection band as well as a broad band are also observed around 715 and 645 nm, respectively, for polarization parallel to the b-axis. It is apparent that the position of the reflection maximum is different, depending on the polarization direction, either parallel or perpendicular to the b axis. This is typical of the Davydov splitting known as the interaction between transition moments and indicates the involvement of exciton coupling in the optical process.

TABLE 2: Calculated and Observed Absorption Spectra



		calculated		observed (Figure 1)	
		λ_{max} (nm)	f	λ_{max} (nm)	mol extinct. coeff (dm^3 mol^{-1} cm^{-1}/10^5) or optical density
solution[a] (D_{2h})	A:	630.8	0.693	664.0	1.44
	B:	646.6	0.727	698.5	1.64
		$\Delta\lambda = 15.8$ (387 cm^{-1})		$\Delta\lambda = 34.5$ (744 cm^{-1})	
β phase[b] (C_i)	B:	690.3	0.837	651.5	1.712
	A:	744.5	0.773	712.0	1.778
		$\Delta\lambda = 54.2$ (1055 cm^{-1})		$\Delta\lambda = 60.5$ (1304 cm^{-1})	

[a] In Cl-naphthalene. [b] Evaporated film.

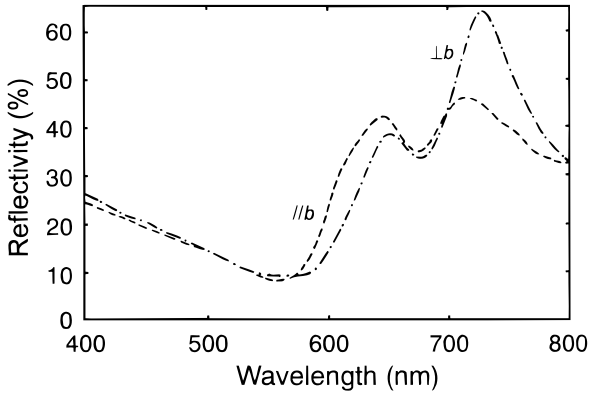


Figure 3. Polarized reflection spectra measured on the (001) plane of a single crystal of β-MfPc.

2.5. Temperature Dependence of Absorption Spectra. In order to separate the effect between molecular distortion and exciton coupling, temperature dependence of the absorption spectra has been investigated in an evaporated film in the range between 20 and 300 K. The result is shown in Figure 4. The shorter-wavelength band around 650 nm is more displaced toward shorter wavelengths on lowering the temperature, whereas the reverse is the case for the longer-wavelength band around 720 nm. However, the extent of the spectral shift is asymmetric and can be explained in the following way.

We assume that the molecular distortion becomes more significant on lowering the temperature, inducing more band splitting in a symmetrical way, as shown by two opposing arrows in Figure 5a. On the contrary, exciton coupling displaces the absorption band toward shorter wavelength. This happens

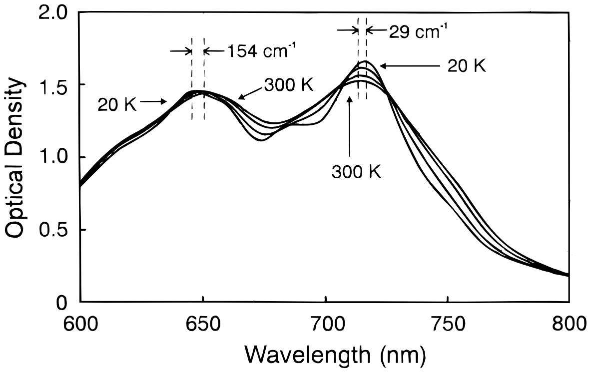


Figure 4. Temperature dependence of absorption spectra in an evaporated film of β-MfPc.

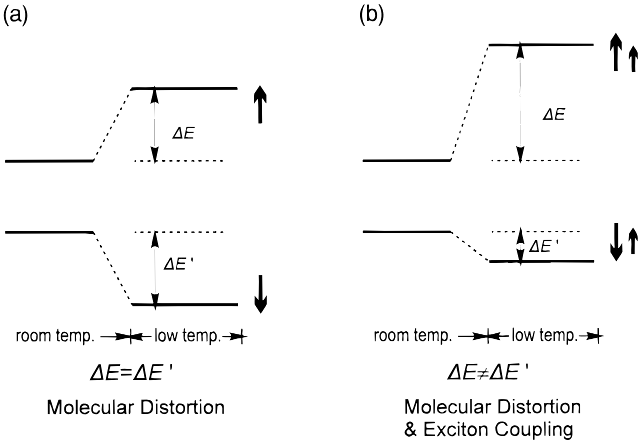


Figure 5. Energy diagram for the temperature effect: (a) due to molecular distortion and (b) due to molecular distortion plus exciton coupling effect (molecular distortion, 92 cm^{-1}; exciton coupling, 62 cm^{-1}).

because the angle between two transition moments is about 58–60° on the average, as calculated from the crystal structure.[9] These angles are larger than the critical angle of 54.7°, which determines the hypsochromic or bathochromic shift.[14,15] Therefore, both temperature effects due to molecular distortion and exciton coupling are superimposed on the actual absorption spectrum, as shown by short and long arrows in Figure 5b. The shorter-wavelength band exhibits an in-phase enhancement, while the longer-wavelength band is an out-of-phase superposition. The contribution of molecular distortion is calculated to be 92 cm^{-1}, whereas the component of the exciton coupling is about 62 cm^{-1}.

3. Summary and Concluding Remarks

The electronic spectra of β-MfPc has been characterized from the standpoint of molecular distortion. The reduction in molecular symmetry from D_{2h} to C_i is recognized on going from solution to the solid state. Molecular distortion is found to enhance the band splitting in such a way that the longer-wavelength band is more displaced toward longer wavelengths while the shorter-wavelength band is more shifted toward shorter wavelengths. The electronic spectra of MfPc can mostly be interpreted in terms of the distortion of molecular framework. However, some exciton coupling effect is also observed in the optical transition, as shown by polarized reflection spectra as well as temperature dependence of absorption spectra.

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