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MOLECULAR DISTORTION AND π-π INTERACTIONS IN THE SOLID STATE OF TITANYLPHTHALOCYANINE

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Abstract The influence of intermolecular interactions on the optical absorption has been investigated in single crystals (phases I and II) and evaporated films (amorphous phase, phases I, II and Y) from the standpoint of molecular distortion and interplanar π-π interactions. Careful re-examination of the X-ray structure analysis revealed that the TiOPc molecules are considerably distorted in phase II (near-IR active) and there are close atomic contacts along the molecular stack. This molecular distortion (reduction in molecular symmetry: $C_{4v} \rightarrow C_1$) lifts the doubly degenerate excited state, giving rise to the two absorption bands (660 and 840 nm) whose transition moments are orthogonal. The major part of the optical absorption spectra in phases I and II can be interpreted in terms of the distortion of molecular framework. Furthermore, the molecular distortion is found to be closely linked with interplanar π-π interactions, as supported by the temperature dependence of absorption spectra and lattice contraction. The correlation between molecular distortion and π-π interactions suggests that the molecule can be distorted in the solid state due to π-π interactions along the molecular stack.

INTRODUCTION

Titanylphthalocyanine (TiOPc) is a well-known, near-IR active photoconductor used practically for GaAsAl-laser printers. A number of investigations have been carried out on electrophotographic properties of TiOPc[1-3] as well as crystal structures (phases I and II[4], and simulated Y-phase[5]) and optical properties[6]. Crystal modifications I, II and Y are known to exist for TiOPc. Among these, phases II and Y are photoactive in the near-IR region. However, the details of the near-IR absorption has not been fully explored yet, especially the correlation between the absorption spectra and crystal structures. Recently, electroabsorption measurements have been performed by Saito *et*

al on evaporated films of amorphous phase and phases I, II and Y in order to distinguish the local excitation (Frenkel exciton) from charge-transfer transition (CT exciton)[6]. They reported that the excited state of phases II and Y are of CT character while the amorphous phase is characterized by Frenkel excitons.

On the other hand, we have recently found that the molecules are considerably distorted in phases I and II on going from solution to the solid state and that this molecular distortion exerts a profound influence on the optical absorption spectra. The purpose of the present investigation is to characterize the near-IR absorption from a molecular-distortion point of view as well as a solid state aspect based on the interplanar π-π interactions.

EXPERIMENTAL

Materials

TiOPc was prepared according to the procedure described in ref.5. The single crystals of phases I and II[4] were grown from the vapor phase using a two-zone furnace[7]. The evaporated films of TiOPc were prepared under high vacuum onto glass substrates (thickness: *ca* 1000 Å). Phase I was obtained by heating the sample in air at 260 °C for 30 minutes. Phases II and Y were prepared by exposing the evaporated films to acetone vapors for one hour and to the mixed vapors of chlorobenzene and water for 24 hours[6], respectively.

Measurements

The temperature dependence of the absorption spectra of TiOPc as well as of the lattice constants was measured in the range of 12-293 K and 83-293 K, respectively. Polarized reflection spectra were measured on single crystals of phases I and II by means of a microscope-spectrophotometer.

Molecular orbital calculations

The INDO/S program employed is part of the ZINDO program package[8]. For the conformation simulation in solution, geometry of the TiOPc molecule was optimized by the INDO/S Hamiltonian. Optical absorption bands were then computed on the optimized geometry using the INDO/S Hamiltonian. Optical absorption bands for the molecule in phases I, II[4] and also in simulated Y-phase[5] (hereafter designated by Y*) were calculated on the basis of x, y, and z coordinate sets[4, 5] using the INDO/S Hamiltonian.

RESULTS AND DISCUSSION

Solution and solid state spectra

Figure 1 shows the solution spectrum of TiOPc in chloronaphthalene as well as solid state absorption spectra of evaporated films for phases "as evaporated", I, II and Y. The near-IR absorption is present in phases II and Y in the form of a very broad band.

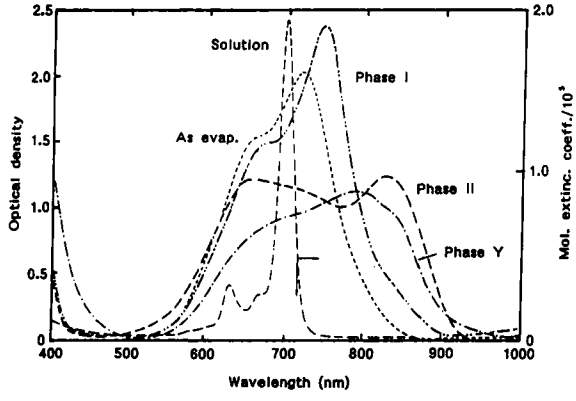


FIGURE 1 Solution and solid state spectra of TiOPc.

Molecular distortion in phases I, II and Y*

The conformation of the TiOPc molecule of phase II is shown in Fig.2[4]. The central Ti ion (TiO^{2+}) is significantly out of the convex molecular plane and forms a square pyramid together with four nitrogen atoms N1, N2, N3 and N4. In order to quantify the extent of molecular distortion in the solid state, we measured the angles between the plane of the four central nitrogen atoms (plane 1) and the plane of each phenyl ring (plane 2) on the basis of the reported structures[4,6]. These angles are listed in Table 1.

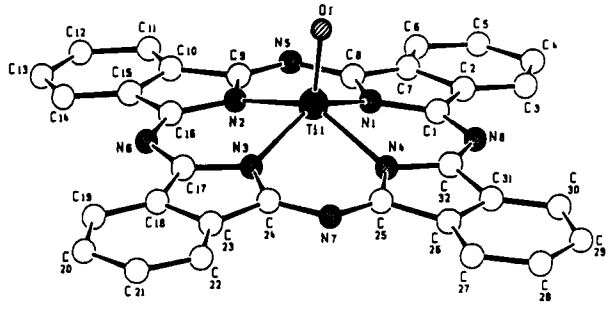


FIGURE 2 Conformation of the TiOPc molecule (phase II).

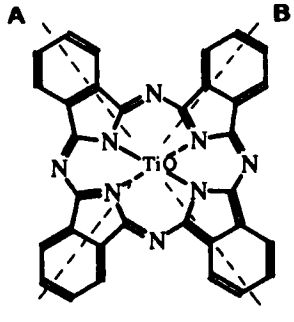
TABLE 1 Molecular distortion of the TiOPc molecule for modifications I, II and Y* and for the conformation optimized by the INDO/S Hamiltonian.

Plane 1	Plane 2	Phase I (C_1)	Phase II (C_1)	Phase Y* (C_1)	Geo. Opt. (C_{4v})
N1,N2,N3,N4	Phenyl C2.....C7	6.1°	7.9°	7.8°	7.1°
"	Phenyl C10...C15	7.7°	11.8°	11.8°	7.1°
"	Phenyl C18...C23	6.5°	6.2°	6.2°	7.0°
"	Phenyl C26...C31	5.8°	1.2°	1.2°	6.8°

In the optimized geometry which corresponds to the conformation in solution, the four angles are almost equal, indicating that there is C_{4v} symmetry. On the other hand, there is no molecular symmetry except for the identity element in phases I, II and Y* (C_1). The molecular distortion in phase I is not so significant; whereas the molecules in phases II and Y* are considerably and equally distorted.

TABLE 2 Computed optical absorption according to the INDO/S method.

	Optical absorption band I [Transition: 97 → 99th orbital]		Optical absorption band II [Transition: 97 → 98th orbital]	
	λ (nm)	f (osc. strength)	λ (nm)	f (osc. strength)
Phase I (C_1)	716.4	0.765	737.8	0.850
Phase II (C_1)	678.8	0.624	775.1	1.023
Phase Y* (C_1)	678.6	0.625	774.5	1.022
Opt. Geo.** (C_{4v})	736.9	0.803	738.0	0.800



Influence of molecular distortion on the optical absorption (MO calculations)

Table 2 shows the computed optical absorption bands together with their oscillator strength for phases I, II and Y* and also for the optimized geometry. The 97th orbital corresponds to the HOMO and the 98th and 99th orbitals are the LUMO. The LUMO is

doubly degenerate due to C_{4v} symmetry in the optimized geometry which corresponds to the conformation in solution. The single visible absorption band observed in solution (Fig.1) agrees with the present calculation.

The major component of the optical absorption band is assigned to the π-π^* transition ($a_2 \rightarrow e$) from the HOMO to the doubly degenerate LUMO. As shown in the inset of Table 2, the transition moments lie on the molecular plane and are orthogonal because the dipole operator components x and y transform according to representation E of C_{4v} symmetry. This degeneracy is however lifted in phases I, II and Y* due to molecular distortion on going from solution (C_{4v}) to the solid state (C_1) to give two optical absorption bands A and B. The band splitting in phase I is relatively small; whereas it becomes larger in phases II and Y* as the molecular distortion is increased.

Polarized reflection spectra measured on single crystals of phases I and II

Figures 3(a) and 3(b) show the polarized reflection spectra measured on the $(\bar{1}00)$ and $(0\bar{1}0)$ planes of the single crystals of phases I and II, respectively. A prominent reflection band appears in phase I at 755 nm together with another one at 680 nm for polarization parallel to the b-axis (nearly the molecular plane). No noticeable dispersion can be observed for polarization perpendicular to the b-axis (nearly parallel to the c-axis of the molecular stack). Polarization experiments were also performed on the molecular plane along the transition moments A and B as shown in the inset of Table 2. The polarizations A and B gave two independent reflection bands at 758 and 775 nm, respectively, in experiments which are not presented here. The difference in these two peaks amounts to 17 nm, and this corresponds to the band splitting in phase I. This agrees well qualitatively with the computed optical absorption bands shown in Table 2.

On the other hand, an intense near-IR reflection band is clearly observed in phase II around 850 nm for polarization perpendicular to the $(a,\bar{c})$-diagonal direction (*i.e.* the molecular plane). In addition, some weak broad bands are recognized in the range from 600 to 900 nm for polarization parallel to the $(a,\bar{c})$-diagonal direction (*i.e.* the molecular stack). These bands are, however, not attributed to intermolecular charge-transfer transitions, but due to small vector components of the transition moment along the molecular stack as shown in Fig.4(a).

Figure 4(a) exhibits the polarized reflection spectra measured on the $(10\bar{1})$ plane (nearly the molecular plane) along the transition moments A and B. Polarizations A and B gave two independent reflection bands at 660 and 840 nm, respectively. The difference in these reflection bands amounts to 180 nm, and this corresponds to the band splitting in phase II. The present result is qualitatively in good agreement with the calculated optical absorption bands shown in Table 2.

Figure 4(b) exhibits the averaged reflection spectrum measured on the $(10\bar{1})$ plane with a polarization angle of 45° with respect to the orthogonal transition moments. This averaged spectrum agrees quite well with the broad absorption spectrum in evaporated films of phase II shown in Fig.1 (see also Fig.7(c) at 12 K).

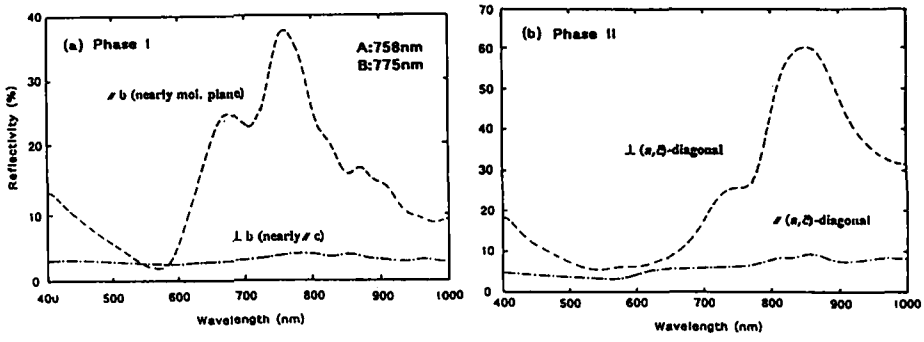


FIGURE 3 Polarized reflection spectra measured on single crystals: (a) on the (100) plane for phase I and (b) on the $(0\bar{1}0)$ plane for phase.

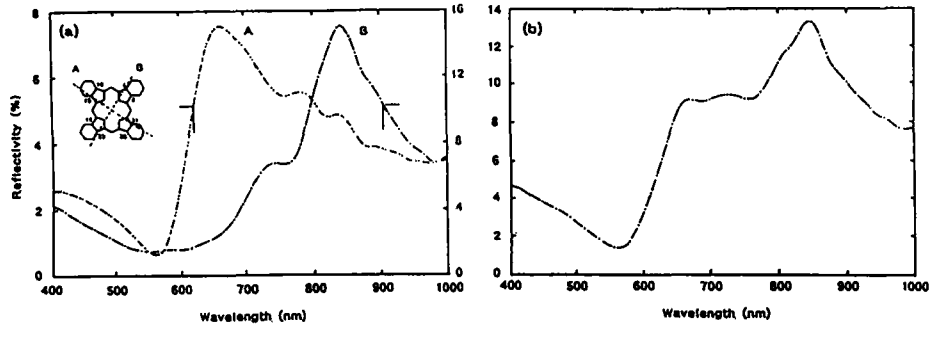


FIGURE 4 Polarized reflection spectra measured on the $(10\bar{1})$ plane (nearly on the molecular plane) of a single crystal of phase II: (a) along the transition moments A and B, and (b) along the diagonal direction between the transition moments A and B.

Atomic Contacts as a Measure for Interplanar π-π Interactions

Figures 5(a) and 5(b) show the convex and concave overlaps for phase II. It is to be noted that there are very close atomic contacts in the N6-N6 (3.145 Å) and C15-C18 (3.391 Å) in the convex pair and N4-N4 (3.504 Å) and C9-C28 (3.211 Å) in the concave pair. These atomic contacts are repeated alternately along the stacking axis ($(a,\bar{c})$-diagonal direction.

The concave overlap in phases I and Y* resembles that of phase II while the convex overlap is quite different as shown in Fig.6, where the molecules are overlapped only at the periphery of the molecule. There are some atomic contacts in the concave and convex pairs in phases I and Y*. However, no equivalent close contacts to those in phase II can be recognized.

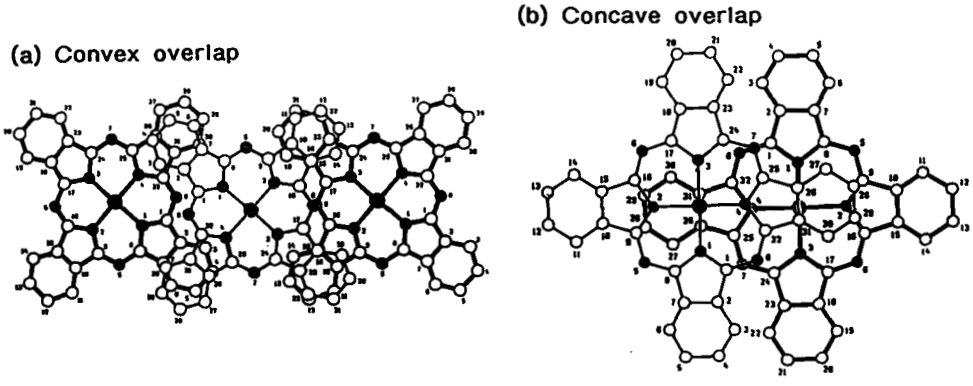


FIGURE 5 Convex overlap (a) and concave overlap (b) in phase II.

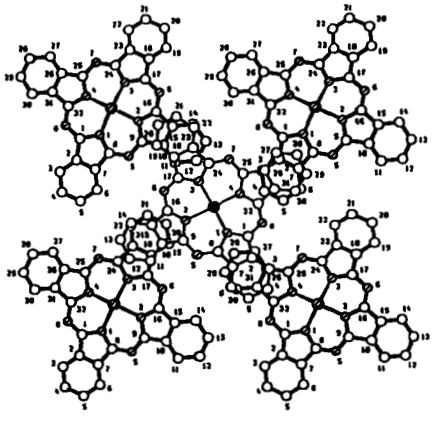


FIGURE 6 Convex overlap in phase I.

Temperature dependence of absorption spectra and lattice contraction

Figures 7(a)-(d) show the temperature dependence of the absorption spectra of evaporated TiOPc for phases "as evaporated", I, II and Y measured in the range between 12 and 293 K. No significant temperature dependence is observed in phases "as evaporated" and I on lowering the temperature. On the other hand, a series of substantial bathochromic shift is clearly observed in the near-IR absorption in phases II and Y, accompanied by enhanced optical absorption intensity. It should be noted that the very broad band in phases II and Y is now resolved into several peaks at 12 K. The absorption spectrum in phase II at 12 K (Fig.7(c)) is very similar to that of the averaged reflection spectrum shown in Fig.4. The present temperature dependence in phases I and II is well correlated with lattice contraction at low temperatures.

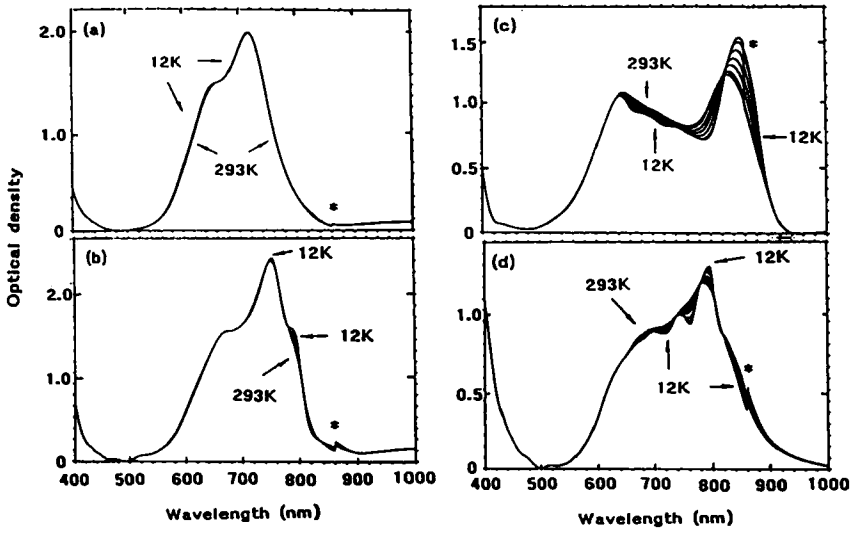


FIGURE 7 Temperature dependence of absorption spectra of evaporated TiOPc: (a) as evaporated, (b) phase I, (c) phase II, and (d) phase Y. The discontinuity denoted by an asterisk (*) is due to a change in detectors.

Figures 8(a) and 8(b) show the temperature dependence of the lattice parameters of single crystals of phases I and II measured in the range between 83 and 293 K. In phase I, the lattice is significantly contracted along the c-axis which is nearly parallel to the molecular stack. Similarly, in phase II, lattice contraction occurs in the $(a,\bar{c})$-diagonal direction which is again along the molecular stack. The present results clearly indicate that the temperature dependence of absorption spectra shown in Figs.7(b) and 7(c) is due to the change in interplanar interactions caused by lattice contraction.

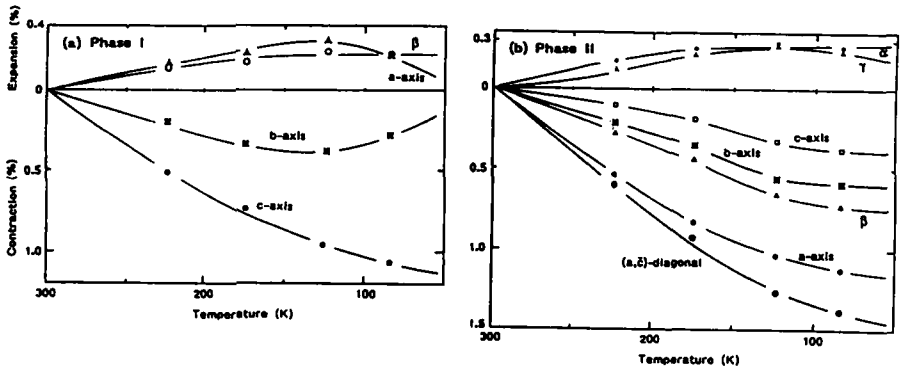


FIGURE 8 Temperature dependence of the lattice parameters measured on single crystals: (a) phase I and (b) phase II.

Correlation between molecular distortion and π-π interactions

In the discussion based on the molecular aspect, we have seen that the optical absorption spectra can be interpreted in terms of the distortion of molecular framework. In fact, molecular distortion, band splitting, MO calculations and polarized reflections spectra are fully consistent, although appreciable intermolecular interactions are operative in the solid state. On the other hand, in the discussion based on the solid-state aspect, we have also found the correlation between molecular distortion and π-π interactions (π-π contacts), indicating that molecular distortion is much more significant in phase II than in phase I, just as the π-π interactions are more considerable in phase II than in phase I.

The above facts prompt us to suggest that the molecules are presumably deformed due to π-π interactions so as to stabilize themselves in the solid state. This allows us to draw an electronic diagram for phases I and II as shown in Fig. 9. The 98 and 99th orbitals are degenerate due to C_{4v} symmetry in solution. This degeneracy is, however, removed due to molecular distortion caused by π-π interactions in phase I. The band splitting becomes still larger in phase II due to enhanced molecular distortion to give, finally, an intense near-IR absorption of 840 nm.

SUMMARY AND CONCLUDING REMARKS

The electronic spectra of TiOPc has been discussed from a molecular point of view as well as a solid state aspect and the conclusion can be summarized as follows.

1. Molecular distortion and π-π interactions are well correlated, and play a dominant role in the electronic state of TiOPc.
2. The reduction in symmetry ($C_{4v} \rightarrow C_1$) due to molecular distortion causes a band splitting, giving two optical absorption bands in the solid state. The band splitting depends largely on the extent of molecular distortion.
3. The molecule in phase II is more distorted than in phase I. This makes a longer-wavelength transition possible.
4. Close atomic contacts in convex and concave pairs are present in phase II, leading to strong interplanar π-π interactions.
5. The near-IR absorption in phase II arises from π-π interactions that are associated with molecular distortion.

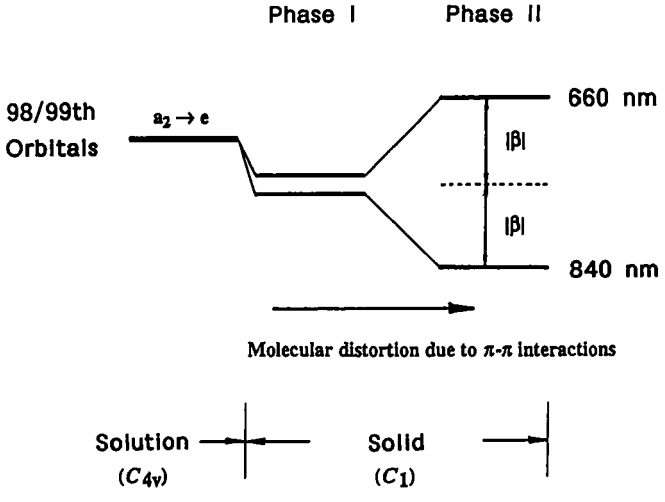


FIGURE 9 A schematic model for the excited state of TiOPc.

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