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Structural and Optical Properties of 5,15-diaza-6,16-dihydroxy-tetrabenzo[*b*,*e*,*k*,*n*]perylene

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ABSTRACT

*5,15-Diaza-6,16-dihydroxy-tetrabenzo[*b,e,k,n*]perylene (DDTP) is a new violet/purple pigment based on the diaza-perylene skeleton. DDTP was found to exhibit two distinct colors in evaporated films: violet and reddish-purple. The violet color is typical of the evaporated sample, while the evaporated sample undergoes a color change to reddish-purple when exposed to the vapors of certain organic solvents. The structural and optical properties of DDTP have, therefore, been investigated in evaporated films and single crystals in order to elucidate the coloration mechanism. X-Ray diffraction diagrams of the evaporated films revealed that there are two crystalline phases which correspond to the above two colors. X-Ray structure analysis on single crystals showed that the molecule is in the enol form and that the two opposing phenyl rings at the corners of the skeleton are bent out of the molecular plane due to steric repulsion. The analyzed structure corresponds to the reddish-purple form, as is also borne out by polarized reflection spectra measured on a single crystal. Although the violet phase looks quite similar to the reddish-purple one, a slight difference in the molecular arrangement induces a change in vibrational–electronic transitions, giving the violet color. © 1997 Elsevier Science Ltd*

Keywords: pigment, diaza-perylene, crystal structure, electronic spectra, phase change, MO calculations.

INTRODUCTION

5,15-Diaza-6,16-dihydroxy-tetrabenzo[*b*,*e*,*k*,*n*]perylene (DDTP) (Fig. 1a) is a new purple/violet, light-stable and insoluble pigment based on the diaza-perylene skeleton. Kitahara *et al.* prepared it from diethyl-2,5-dioxo-1,4-cyclohexane-dicarboxylate and 2-amino-benzophenone and claimed a patent with a keto structure [1]. The color of the pigment was reddish-purple in polymer matrix. Later, Kitahara and Nishi reported in detail on the synthesis of diaza-perylene derivatives [2]. They proposed three possible structures, namely, an enol structure (Fig. 1a), a keto structure, as well as 5,15-diaza-5*b*,15*b*-dihydrotetrabenzo[*b*,*e*,*k*,*n*]-perylene-6,16-dione. Of these, they selected the last structure, as they could observe neither NH nor OH stretching bands in the IR spectra. Independently, Jaffe prepared the same substance by essentially the same synthetic route and claimed a patent with the aforementioned keto structure [3]. The color was, however, black-violet. In view of the above, single crystals were grown from the vapor phase in order to determine the molecular and crystal structures [4]. The X-ray analysis supported the enol structure as shown in Fig. 1(a), contrary to the proposed two structures.

In the course of studies on the optical properties of DDTP, it was found that DDTP exhibits two distinct colors in evaporated films: reddish-purple and violet. The violet color is typical of the evaporated sample, whereas the reddish-purple color appears when the evaporated film is exposed to the

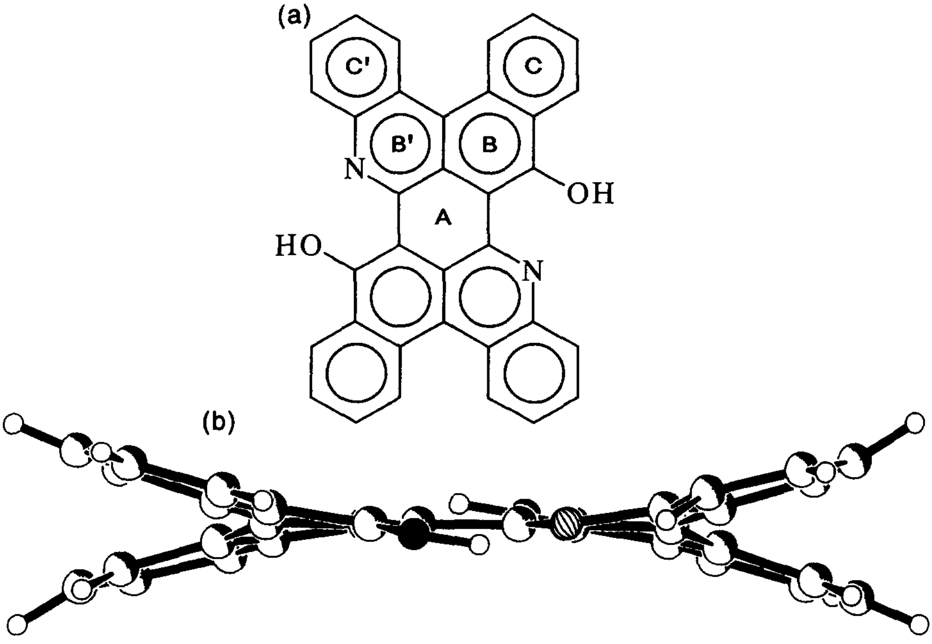

Fig. 1. Conformation of the DDTP molecule (C_i): (a) top view and (b) side view. Rings A and C are planar, while ring B is heavily deformed.

vapors of certain organic solvents. In order to clarify the two different colors in the solid state, an investigation was carried out on evaporated films and single crystals on the basis of the crystal structure and intermolecular interactions.

EXPERIMENTAL

Synthesis and crystal growth of single crystals

DDTP was prepared according to the method previously described [3]. The powdered DDTP was purified twice by vacuum sublimation using apparatus described previously [5]. The single crystals were then grown from the vapor phase using the same sublimation equipment [4]. DDTP was sublimed at about 635 K, and the argon flow rate was controlled at 10 mm^3 s^{-1} using a mass flow meter (F-100/200, Bronkhorst BV). After 48 h of vapor growth, a number of lustrous acicular platelets were obtained.

Preparation of evaporated films

The evaporated films of DDTP were prepared under high vacuum using conventional evaporation equipment. The samples were made on plain glass substrates for measurements of the X-ray diffraction diagrams and visible spectra, and on a KBr disk for measurements of the IR spectra. The color of the evaporated samples was violet. The reddish-purple sample was obtained by exposing the evaporated films to acetone vapor for 1 h, as it is often employed for color changes in organic pigments [6].

Measurements

Visible absorption spectra were recorded on a UV/NIR Lambda 9 spectrophotometer (Perkin–Elmer). The temperature dependence of the absorption spectra of evaporated DDTP was measured in the range between 12 and 293 K in combination with a Displex cryostat from Air Products. Lattice constants of the single crystal were measured in the temperature range between 83 and 293 K with a Philips PW1100 diffractometer in combination with a NCD1 cryostat from Leybold–Heraeus. Polarized reflection spectra were measured on single crystals of DDTP by means of a UMSP80 microscope–spectrophotometer (Carl Zeiss) equipped with an R2658 photomultiplier (HTV). An Epiplan Pol (×8) objective was used together with a Nicol-type polarizer. Reflectivities were corrected relative to the reflection standard of silicon carbide.

Molecular orbital (MO) calculations

Geometry of the DDTP molecule was optimized by the AM1 Hamiltonian in MOPAC93 [7] in order to simulate the conformation in solution. The INDO/S program employed for spectroscopic calculations is part of the ZINDO program package [8]. The CNDO/S program used was a modified version of the CNDO/2 (QCPE #141) to include the configuration interaction [9]. PPP calculations were also carried out, using the variable β (resonance integral), γ (electron repulsion)-approximation. The standard parameters were taken from ref. [10] except for the nitrogen values for the NH group ($I_p = 23$ eV and $\gamma_{rr} = 17.44$ eV). The Mataga–Nishimoto [11] equation was used for the evaluation of the electronic repulsion integral in all calculations: 400, 99 and 60 configurations were considered for the configuration interaction (CI) for the INDO/S, CNDO/S and PPP calculations, respectively. All optical absorption bands were calculated on the optimized geometry using an RS6000 IBM-workstation.

RESULTS

Molecular conformation and crystal structure

Figure 1(a) shows the conformation of the DDTP molecule which belongs to point group C_i. The DDTP molecule is overcrowded at the four corners, and

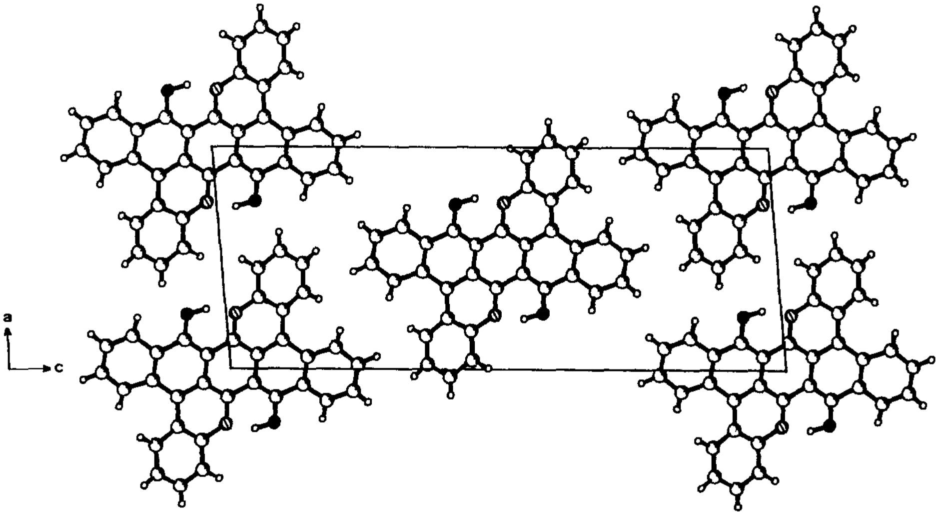

Fig. 2. Projection of the crystal structure of DDTP on the (*a*,*c*) plane.

the two inner opposing hydrogen atoms in phenyl rings C and C′, for example, repel each other. This results in a deviation of the phenyl ring from the perylene-skeleton in such a way that one ring (ring C, for example) is above the molecular plane while the other (ring C′) is below it, as shown in Fig. 1(b). Phenyl rings A and C (C′) are planar, while ring B (B′) is heavily deformed. There are intramolecular hydrogen bonds between the OH group and the N atom which stabilize the molecule.

The crystal data for DDTP [4] are: monoclinic, $P2_1/n$, $a=10.599(1)$, $b=3.775(1)$, $c=26.517$ Å, $\beta=95.17(1)°$, $V=1056.7(3)$ Å^3, $Z=2$. Figure 2 shows the projection of the crystal structure on the (a,c) plane. The molecules are stacked in a herringbone fashion along the b axis with an interplanar distance of 3.40 Å.

Solution and solid-state spectra

Figure 3 shows the solution spectrum of DDTP in dimethylsulfoxide (DMSO). It is apparent that the absorption bands in the visible region are almost equally spaced (separation: about 1450 cm^{-1}), indicating a progression of absorption bands. This implies that these bands are due to vibrational structures of the electronic band. This present interpretation will be substantiated by polarized reflection spectra measured on a single crystal, as described below.

Figure 4 shows the absorption spectra of evaporated DDTP before and after vapor treatment. The absorption spectrum as evaporated gives a

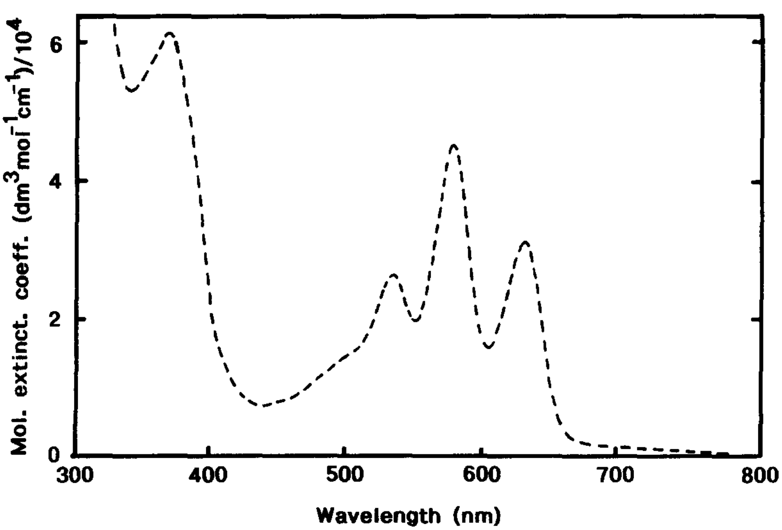

Fig. 3. Optical absorption spectrum of DDTP solution in DMSO.

violet color and is very similar in shape to the solution spectrum (Fig. 3). This indicates that the component molecules of the crystal preserve their individuality. Vapor treatment then transforms the violet color to reddish-purple in such a way as to induce a large intensification of the absorption band at about 556 nm relative to that of the band at 600 nm. On the other hand, the longest wavelength band at about 660 nm is slightly displaced towards longer wavelengths by about 20 nm, accompanied by reduction in absorption intensity.

As is evident from the spectra (Fig. 4), it is the relative absorption intensity of the bands at 556 and 600 nm that determines the color, i.e. whether it is violet or reddish-purple, because human eyes are very sensitive to this wavelength region.

X-Ray diffraction diagrams

Figure 5 shows the X-ray diffraction diagrams before and after vapor treatment. Before vapor treatment, there is only one prominent peak at $2\theta = 7.2°$ which is not assignable on the basis of the analyzed crystal structure [4]. The very broad peak around 23° is due to the glass substrate used. Vapor treatment makes the peak at $2\theta = 7.2°$ disappear. Instead, two new diffraction peaks appear at $2\theta = 6.6$ and $8.6°$ which are attributed to the (002) and

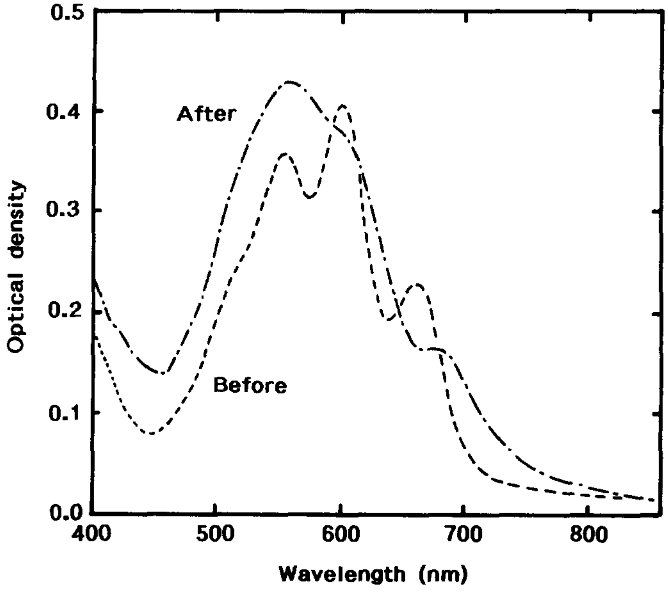

Fig. 4. Optical absorption spectra of evaporated DDTP before and after vapor treatment (film thickness: 800 Å).

($-\bar{1}01$) planes of the crystal structure mentioned above [4]. The change in diffraction diagrams due to vapor treatment is indicative of the phase change.

IR spectra of evaporated DDTP

Figure 6 shows the IR spectra of evaporated DDTP before and after vapor treatment. The absorption band around 3050 cm^{-1} is due to the hydrogen-bonded OH stretching vibration between the OH group and the N atom. This band is greatly displaced towards lower wavenumbers as compared with the free OH stretching band (~3500 cm^{-1}) and is also characterized by a rather narrow band. The narrow band is typical of the intramolecular hydrogen bond because the hydrogen atom cannot fluctuate in a wide range. In contrast, the hydrogen atom in the intermolecular hydrogen bond can be distributed more widely between two hydrogen-bond-forming atoms, thus giving a fairly broad band, as is well known.

The bands in the region between 1400 and 1600 cm^{-1} are ascribed to the C—C stretching of the aromatic phenyl and pyridine rings. In this region, one can see some changes in absorption bands caused by vapor treatment. The medium band around 1210 cm^{-1} is attributed to the C—O stretching vibration of the phenol type. A slight change around 965 cm^{-1} is also recognized and can be assigned to the OH 'out of plane' vibration. The small band around 1760 cm^{-1} always appears as a result of vapor treatment, accompanied by a change in C—O stretching band around 1210 cm^{-1}. This band is assignable to the C=O stretching vibration, but it seems contradictory to the enol form of DDTP.

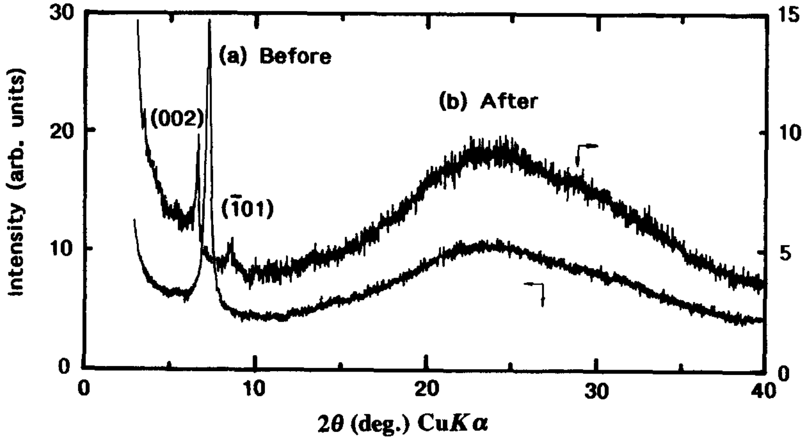

Fig. 5. X-Ray diffraction diagrams of evaporated DDTP before and after vapor treatment (radiation: CuKα). The broad band around $2\theta = 26°$ is due to the glass substrate used.

Temperature dependence of absorption spectra and lattice contraction at low temperatures

Lattice contraction enhances intermolecular interactions because of the shortening of the intermolecular distance. The resulting enhanced interaction is then expected to induce some changes in optical absorption bands. Figure 7(a) and (b) show the temperature dependence of evaporated DDTP before and after vapor treatment. Before vapor treatment, the three main absorption bands at 565, 600 and 660 nm exhibit the hyperchromic effect (intensification of optical absorption) at low temperatures, accompanied by slight hypsochromic displacements. Several isosbestic points can also be recognized in the spectra, indicating that the spectral changes may be based on a binary equilibrium system. Similarly, several isosbestic points are also observed in the absorption spectra after vapor treatment, as shown in Fig. 7(b). The absorption band at 600 nm is substantially intensified as the temperature is decreased, the bands at 556 and 680 nm to a lesser extent.

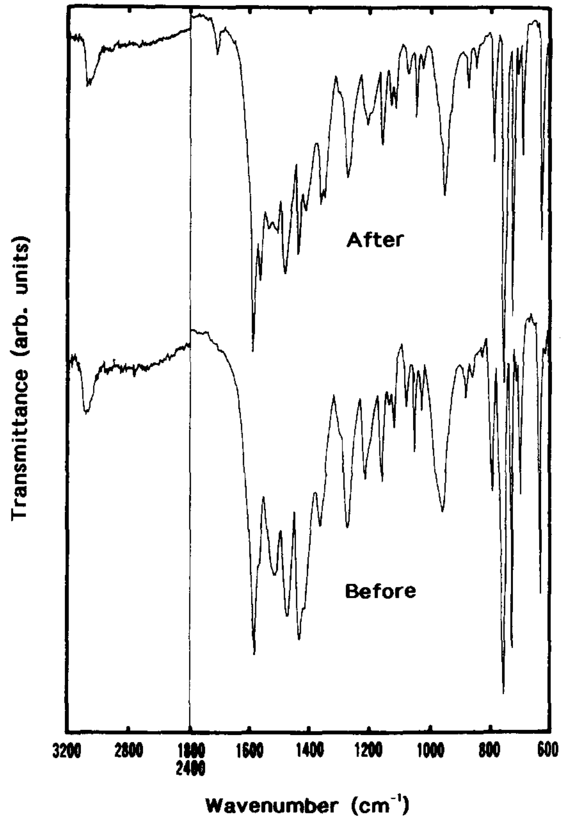

Fig. 6. IR spectra of evaporated DDTP before and after vapor treatment.

Figure 8 shows the temperature dependence of the lattice parameters of a single crystal measured in the range between 83 and 293 K. It is remarkable that the lattice is exponentially contracted along the stacking *b* axis, whereas the lattice contraction along the *a* axis becomes almost constant at 173 K. The contraction along the *c* axis appears to be oscillating.

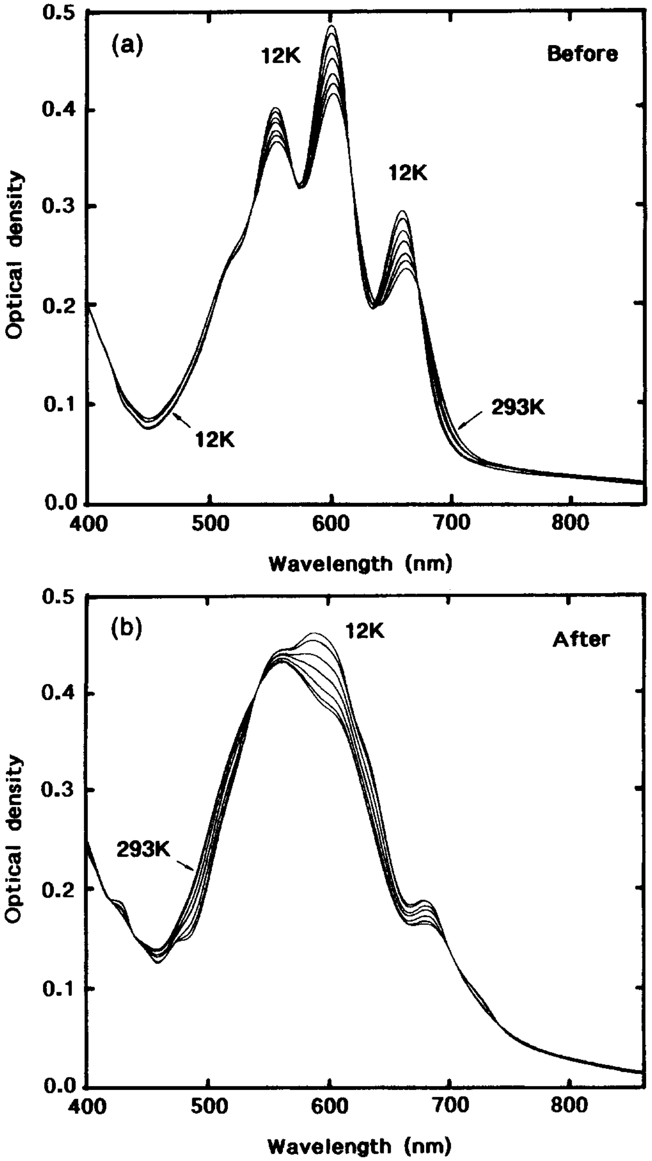

Fig. 7. Temperature dependence of the absorption spectra of evaporated DDTP: (a) before and (b) after vapor treatment (film thickness: 800 Å).

Polarized reflection spectra measured on a single crystal

Figure 9 shows the polarized reflection spectra measured on the ($\bar{1}01$) plane of a single crystal of DDTP. A prominent broad reflection band appears around 580 nm together with a smaller band at 680 nm for polarization perpendicular to the *b*-axis, whereas no dispersion can be observed for polarization parallel to the *b*-axis. On the ($\bar{1}01$) plane, the *b* axis is perpendicular to the (*a*,*c*)-diagonal direction and the molecules are arranged inclined, as can easily be pictured from Fig. 2. The (*a*,*c*)-diagonal direction coincides exactly with the direction of the calculated transition-moment described below, as shown in the inset of Fig. 9. It follows that the electronic bands in the visible region are polarized along the direction of the transition moment ((*a*,*c*)-diagonal)) and these bands disappear completely on irradiation with polarized light perpendicular to the direction of the transition moment (i.e. parallel to the *b* axis). This result evidently indicates that there is only one electronic transition in the visible region and that the absorption bands at 600 and 565 nm are attributed to the vibrational structures of the electronic band. The molecular vibration of about 1450 cm^{-1} is coupled with the pure electronic transition at 700 nm (0–0 transition) and this forms a progression of the vibronic bands.

Computed optical absorption bands and the direction of the transition moment

Table 1 shows the optical absorption bands together with oscillator strength calculated from the INDO/S, CNDO/S and PPP Hamiltonians. All calculations gave the single absorption band in the visible region as well as the same

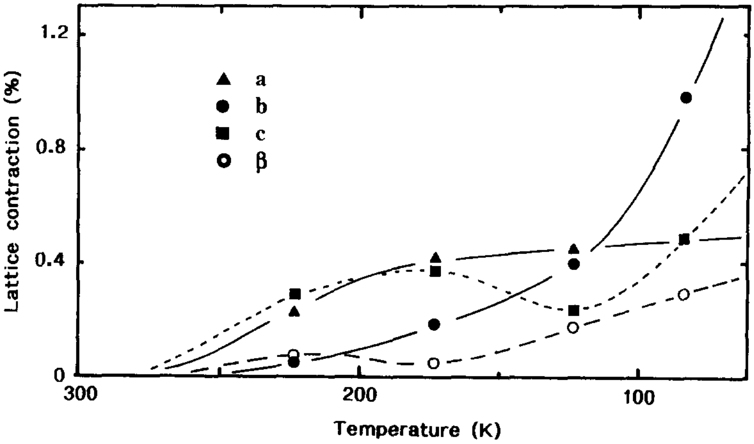

Fig. 8. Temperature dependence of the lattice parameters measured on a single crystal of DDTP.

direction of the transition moment as shown in the inset of Fig. 9 as a dotted line. In these calculations, the absorption bands appear around 420–465 nm and the major component of the optical transition is attributed to the π–π^* HOMO (highest occupied molecular orbital)/LUMO (lowest unoccupied molecular orbital) transition.

Diffuse reflectance spectrum of powdered DDTP

Fig. 10 shows the diffuse reflectance spectrum of powdered DDTP diluted with barium sulfate, the spectrum is corrected using the Kubelka–Munk equation. The present spectrum bears a strong resemblance to the polarized reflection spectra measured on a single crystal (Fig. 9). In fact, the X-ray powder diffraction analysis showed that the powdered phase coincides with that of the single crystal within experimental error.

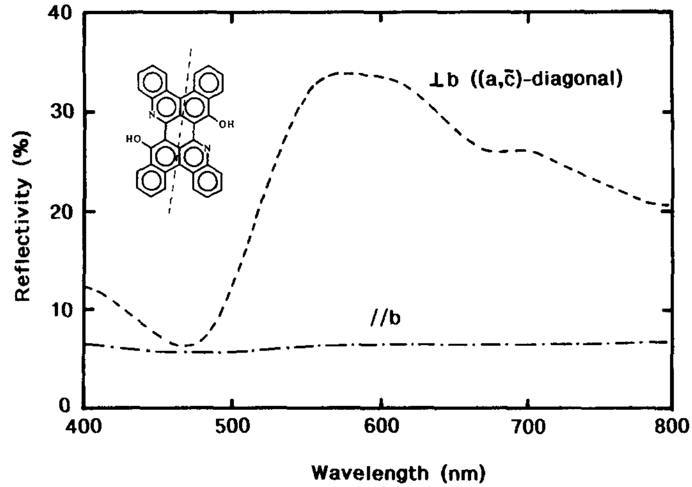

Fig. 9. Polarized reflection spectra measured on the $(\bar{1}01)$ plane of a DDTP single-crystal. The direction of the calculated transition moment is represented by a dotted line on the DDTP molecule in the inset.

TABLE 1
Optical Absorption Bands Calculated from the INDO/S, CNDO/S and PPP Hamiltonians

Hamiltonian	*Wavelength (nm)*	*Oscillator strength*
INDO/S	452.5	0.812
CNDO/S	420.0	0.900
PPP	463.3	1.049

The INDO/S, CNDO/S and PPP calculations gave the same direction of the transition moment as shown in the inset of Fig. 9 as a dotted line.

Two colors in the polymer matrix

The two colors, which correspond to the two different absorption spectra in Fig. 4, appear in different polymer matrices. The pigment-dispersed layer in ABS (acryl–butadiene–styrene)-copolymers, for example, exhibits a reddish-purple color, whereas the violet color is apparent in polycarbonate polymers.

DISCUSSION

Molecular rearrangement ('phase change') due to vapor treatment

The X-ray diffraction diagrams in Fig. 5 provides powerful evidence that the molecules rearrange themselves as a result of vapor treatment ('phase change'). This is also borne out by changes in the IR absorption spectra, which involve spectral shifts and splitting of the band (Fig. 6). These results indicate that the molecular environment has been changed due to vapor treatment.

The phase change mechanism due to vapor treatment is not yet fully understood. We believe that the solvent vapor, because of its modest DDTP-solubilizing power, may loosen the crystal lattice, thus allowing the mole-

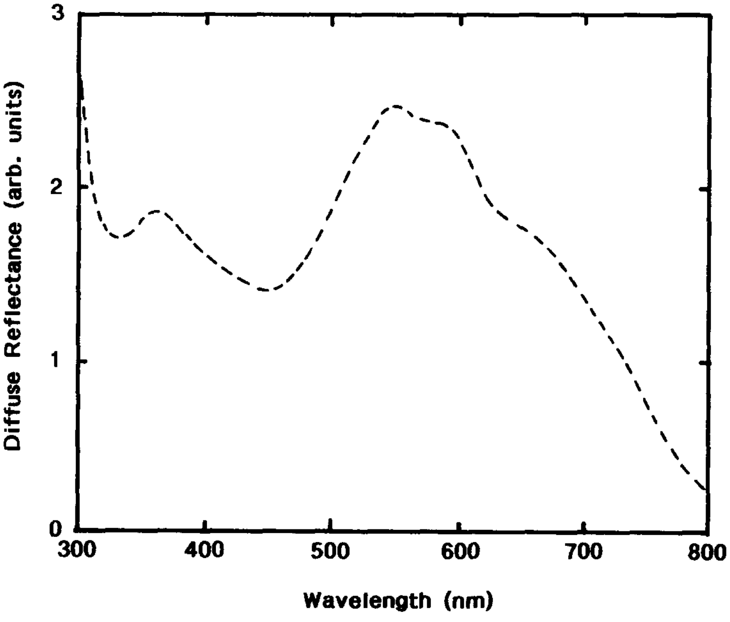

Fig. 10. Diffuse reflectance spectrum of powdered DDTP diluted with barium sulfate.

cules to slide and/or rotate to find an energetically more stable arrangement. A solvent whose DDTP-solubilizing power is extremely low, fails to cause the phase transition, because the solvent cannot loosen the lattice enough. On the contrary, a solvent with a high DDTP-solubilizing power cannot induce the phase change either, because it dissolves the material. So the phase transition, by means of the solvent vapor, is usually caused by a solvent whose DDTP solubility is moderate.

Vibronic transitions in the visible region

The polarized reflection spectra measured on a single crystal (Fig. 9) revealed that there is only one single electronic transition in the visible region and that the direction of the transition moment is along the (*a*,*c*)-diagonal. These results are in good agreement with those obtained by MO calculations (Table 1). It follows that the optical absorption bands in the visible region (Fig. 4) are vibronic transitions, in which a molecular vibration of about 1450 cm^{-1} is coupled with the pure electronic transition at 660 nm (0–0 transition), forming a progression of 600 nm (0–1 transition), 556 nm (0–2 transition) and 515 nm (0–3 transition).

The correlation between the temperature dependence of absorption spectra (Fig. 7b) and lattice contraction (Fig. 8) shows that the optical absorption intensity of the vibronic transition at 600 nm is significantly intensified due to the lattice contraction along the stacking *b* axis on lowering the temperature. This indicates that the transition probability for each vibronic transition can be influenced by changes in molecular environment, leading to a different absorption spectrum.

On the other hand, the absorption spectrum as evaporated (Fig. 7a) shows no significant spectral shift on lowering the temperature. This implies that the molecular nature, as apparent from the strong resemblance in the absorption spectra in solution (Fig. 3) and in the solid state (Fig. 4), is further preserved even at low temperatures and remains unperturbed by molecular environment. Figure 7(a) is also characterized by the hyperchromic effect. This pure intensification of the absorption band can be explained as being due to the increased electron population in the ground state as the temperature is decreased.

As is evident from the above, the color of DDTP is sensitive to the molecular surrounding. It is therefore likely that the two different colors (violet and reddish-purple) appear in different polymer matrices, depending on the environment around the molecule. In other words, the type of polymers (classes, polarity, etc.) as well as the solvents used for the preparation of pigment-dispersed layers play an important role in determining the color in polymer matrix.

CONCLUSIONS

The structural and optical properties of DDTP have been investigated in evaporated films and single crystals with special attention given to the two different colors in the solid state. Two crystalline phases were found to exist in evaporated films, which correspond to two different colors. Polarized reflection spectra on a single crystal revealed that there is only one single electronic transition in the visible region, in good agreement with the prediction given by the MO calculations. These results clearly indicate that all bands are due to vibronic transitions, in which a molecular vibration of about 1450 cm^{-1} is coupled with the pure electronic transition at 660 nm ((0–0 transition), forming a progression of the bands occurring at 600, 556 and 515 nm. The spectral shift or the intensity change of absorption bands caused by vapor treatment depends on the molecular environment. The violet color appears when the (0–1) transition is stronger relative to the (0–2) transition at 556 nm; whereas the reddish purple color is obtained when the reverse is the case.

REFERENCES

1. Kitahara, K., Nishi, H., Hasegawa, M. and Maeda, S., *JP Kokai* (1988) 63-193960.
2. Kitahara, K. and Nishi, H., *Journal of Heterocyclic Chemistry*, **25** (1988) 1063.
3. Jaffe, E. E., US Patent, 1991, 5,028,643.
4. Mizuguchi, J., *Acta Crystallographica*, **C52** (1996) 2315.
5. Mizuguchi, J., *Kristall und Technik*, **16** (1981) 695.
6. Mizuguchi, J., Rihs, G. and Karfunkel, H. R., *Journal of Physical Chemistry*, **99** (1995) 16217.
7. Stewart, J. J., *MOPAC93* (Fujitsu).
8. Zerner, M. C., *ZINDO, A General Semi-Empirical Program Package*. Department of Chemistry, University of Florida, Gainesville, FL.
9. Takata, S., Ono, Y. and Ueda, Y., *Chemical Pharmaceutical Bulletin*, **33** (1985) 3077.
10. Kogo, Y., Kikuchi, H., Matsuoka, M. and Kitao, T., *Journal of the Society of Dyers and Colourists*, **96** (1980) 475.
11. Mataga, N. and Nishimoto, K., *Zeitschrift für Physikalische Chemie*, **13** (1957) 140.