Electronic Structure of the cis and trans Isomers of Benzimidazo Perylene Derivatives and their Use as Black Pigments

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Abstract

Peryleneimide compounds are industrially important pigments in paint industries as well as in electronics areas. We have focused on the title compound (BIP) as a potential substitute for carbon black used widely as the black pigment. For this reason, electronic characterization of the cis and trans form of BIP has been carried out on the basis of the crystal structure and intermolecular interactions. The black color is characterized by two absorption bands in the visible region in both isomers: the former, shorter-wavelength band is due to individual molecules and the latter, longer-wavelength band appears as a result of excitonic interactions between transition dipoles. The stack molecule-pairs, among others, play the determinant role in the appearance of the longer-wavelength band to cover the whole visible region together with the molecular band.

Introduction

Carbon black (CB) is an excellent black pigment on the market and widely used as the materials for printing inks, paints, toners for electrophotography as well as the reinforcing materials for tires.[1] CB is low-cost and extremely light and heat stable, as also characterized by a high hiding power. Because of this, CB is regarded as the perfect black pigment. However, it has recently been pointed out that some types of CB include benzpyrene and other impurities that enhance the risk to induce cancers. There is another issue concerning the inherent nature of the electrical conductivity of CB. An electrically-insulating black pigment is appropriate for LCD color filter applications where the pigment layers (red, green, blue and black) are directly prepared on thin-film transistors (TFT). There is also a demand for an IR-absorption-free, black pigment, because the pigment-dispersed layers (exposed often to the sunshine in the open air) accumulate heat, leading easily to the deterioration of polymers used as vehicles.

For reasons described above, an environmentally friendly, electrically-insulating black pigment with no IR absorption is strongly asked for.

Organic pigments are molecular crystals and thus generally good insulators. However, it is not an easy task to cover the whole visible region with a single-component system of molecules. However, our in-depth study on the electronic structure of peryleneimide pigments revealed that the shade of perylene pigments are characterized by two absorption bands in the visible region: one is due to individual molecules and the other is due to intermolecular interactions.[2,3] So we believed that we could cover the whole visible region with these bands and initiated our search

for those perylene derivatives which satisfy our requirement. Then, we encountered the title compound (BIP[4-6]; Fig. 1). This paper deals with the electronic structure of the cis and trans isomers of BIP on the basis of the crystal structure and intermolecular interactions.
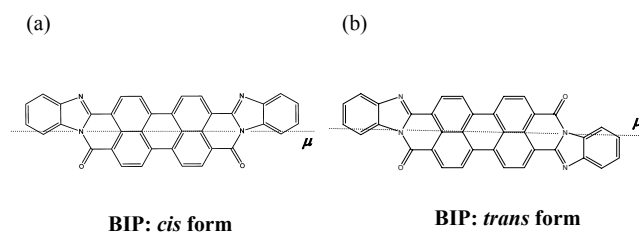

Figure 1. Molecular conformation of BIP: (a) cis form and (b) trans form. The direction of the transition dipole is designated by dotted lines.

Preparation of BIP and Crystal Growth of the cis and trans Isomers

BIP was synthesized by reaction of perylenetetracarboxylic dianhydride with 1,2-phenylenediamine in phenol at 483 K for 6 hours.[6] The products contained both cis and trans isomers of BIP. The isomers were separated by chromatography using a carrier based on a mixed solvent of trifluoroacetic acid and toluene. BIP powders of each form were then purified twice by sublimation under argon at about 675 K, using a two-zone furnace.[7] Single crystals of both forms were grown from the vapor phase in a closed system at about 650 K.

Results and Discussion
Solution Spectra

Figure 2 shows the solution spectra of the cis and trans isomers in dimethylsulfoxide (DMSO). The absorption maximum of the cis form is located at slightly longer wavelengths than that of the trans one. This agrees with the results of MO calculations. Both spectra exhibit a typical progression of absorption bands starting from around 605-610 nm with a spacing about 1400 cm^{-1}. MO calculations showed that there is only one π-π* electronic transition in the visible region, so that the longest-wavelength band is attributed to the pure electronic band as designated by 0-0, followed by the 0-1, 0-2 and 0-3 vibronic transitions as shown.
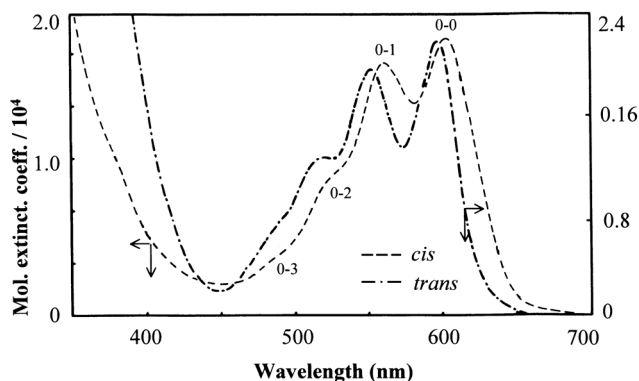
Figure 2. Solution spectra of the trans and cis forms in dimethylsulfoxide.

Structure Analysis

Table 1 details the crystallographic parameters of the *cis* and *trans* forms of BIP. The structure of the *trans* form is similar in lattice parameters to that of the *cis* form, but the former lattice is approximately half of the latter. The *cis* form crystallizes in space group of $P2_1/c$ while the *trans* one in P-1. The molecule has C_i symmetry in the *trans* form. On the other hand, the symmetry of the *cis* form is C_{2v} symmetry. The present symmetry is obviously not compatible with space group $P2_1/c$. This is due to disordered atoms at the corner of the molecule, giving a pseudo center of symmetry.

Figures 3(a) and 3(b) are the projection of the *cis* form onto the (*b,c*) plane and the overlap of two molecules, respectively. The molecules are arranged in a zigzag fashion along the *b*-axis. Two molecules are overlapped with a slip angle of about 46° and the interplanar distance of about 3.20 Å. Likewise, the projection of the *trans* form onto the (*b,c*) plane and the overlap of two molecules are shown in Figs. 4(a) and 4(b), respectively. All molecules are oriented in the same direction in the *trans* form, in contrast to that of the *cis* form. The slip angle as well as the interplanar distance of the overlapped molecules are nearly the same as those of the *cis* form.

Table 1: Crystallographic Parameters for the *cis/trans* Forms

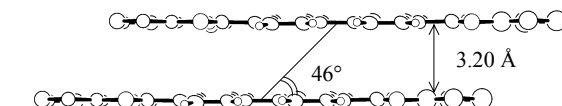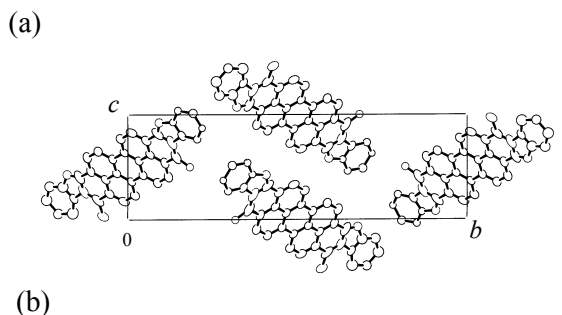|	*cis* form	*trans* form
Formula	$C_{36}H_{16}N_4O_2$	$C_{36}H_{16}N_4O_2$
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
Molecular symmetry	C_{2v}	C_i
Z	2	1
a (Å)	4.7501(6)	4.729(2)
b (Å)	28.079(3)	8.282(2)
c (Å)	8.728(1)	14.693(4)
α (°)	-	89.35
β (°)	99.21(1)	91.15(3)
γ (°)	-	104.83(3)
Density (g/cm³)	1.551	1.602

(a)

(b)

Figure 3. (a) Projection of the crystal structure of the cis form onto the (b,c) plane and (b) overlap of two molecules.
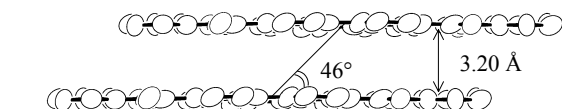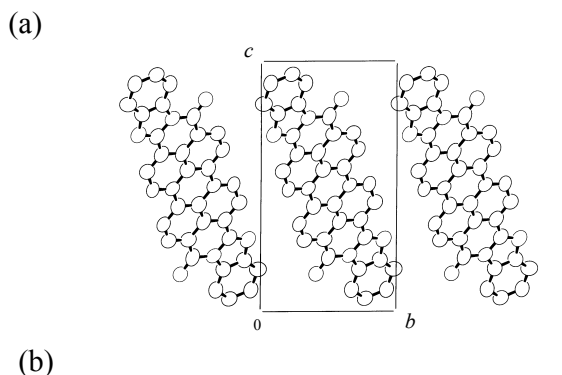
(a)

(b)

Figure 4. (a) Projection of the crystal structure of the trans form onto the (b,c) plane and (b) overlap of two molecules.

Polarized Reflection Spectra Measured on Single Crystals

Figures 5(a) and 5(b) show the polarized reflection spectra of the *cis* form measured on the (*a,c*) plane of single crystals together with the corresponding projection. Polarized light was introduced in parallel or perpendicular to the long molecular axis; *i.e.* the direction of the transition dipole as deduced from MO calculations (Fig. 1). As shown in Fig. 5(a), two intense bands appear around 520 and 700 nm for polarization along the long molecular axis. On the other hand, these reflection bands are completely quenched for polarization perpendicular to the long molecular axis.
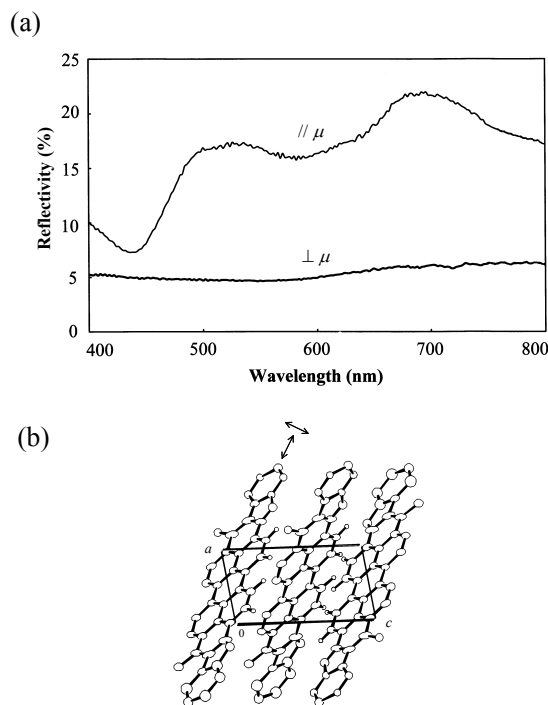
(b)

Figure 5. (a) Polarized reflection spectra of the cis form measured on the (a,c) plane of single crystals and (b) projection onto the (a,c) plane.

(b)

Figure 6. (a) Polarized reflection spectra of the trans form measured on the (a,c) plane of single crystals and (b) projection onto the (a,c) plane.

The present result clearly indicates that the direction of the transition dipole points along the long molecular axis. Furthermore, the band around 520 can be attributed to individual molecules on the basis of our previous results[2,3]; whereas the longer-wavelength band is due to interactions between transition dipoles. The former molecular band is slightly displaced toward shorter wavelengths as compared with that in solution, as is always the case in perylene pigments when an exciton coupling is involved in the optical process. [2,3]

A similar spectroscopic behavior is also observed in polarized reflection spectra of the *trans* form as shown in Fig. 6. In the *trans* form, the reflection maxima are present at slightly shorter wavelengths than those in the *cis* form: around 490 and 690 nm. This tendency is in accord with the molecular spectra in solution (Fig. 2) as well as in MO calculations.

Diffuse Reflectance Spectra

Polarized reflection spectra shown above are typical of one extreme case of the whole spectra, as measured by polarized light on a specific crystal plane. More averaged information is given by diffuse reflectance spectra measured on powders.

Figure 7 shows the diffuse reflectance spectra of the powdered *cis* and *trans* forms. Both spectra are found to cover the whole spectral range in the visible region, showing a black color. It is also to be noted that the spectrum of the *trans* form is more structured and that the reflection maxima of the *cis* form are slightly displaced toward longer wavelengths than those of the *trans* form, as in the case of solution spectra and polarized reflection spectra.
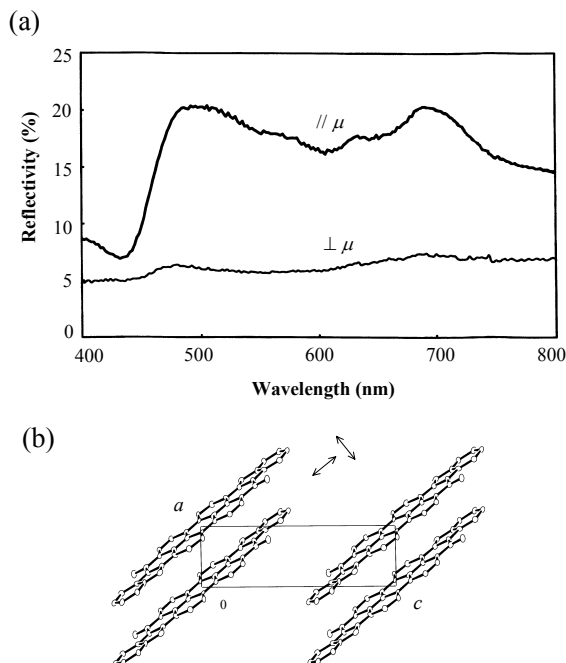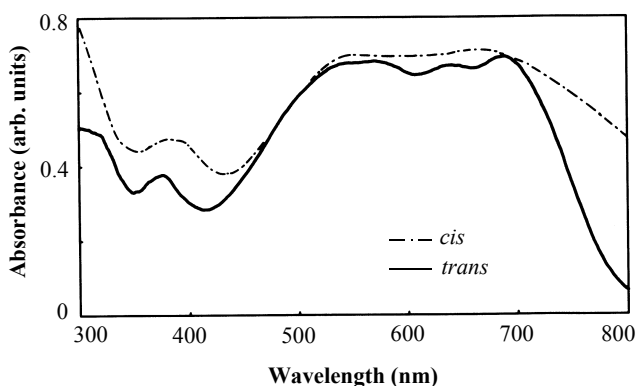

Figure 7. Diffuse reflectance spectra of the cis and trans forms.

Excitonic Interactions Between Stack Pairs

We have pointed out in our previous investigations the importance of the excitonic interactions in pigments,[2,3] in which the absorption coefficient of the component molecule is quite large. The interaction energy ($\Delta E_{exciton}$) is given by the dipole-dipole equation[10,11]: $\Delta E_{exciton} = |\mu|^2(1-3\cos^2\theta)/r^3$, where the transition dipole is denoted by μ, the distance and angle between two transition dipoles by r and θ, respectively.

Now, we examine the extent of the exciton coupling for molecules pairs in the lattice. As judged from the geometrical term $(1-3\cos^2\theta)/r^3$ for the nearest molecule pairs on the molecular plane (Figs. 3(a) and 4(a)) as well as along the stacking axis (Figs. 3(b) and 4(b)), it is evident that the excitonic contribution of the stack

pairs is, by far, larger than that of the pairs on the molecular plane by two orders of magnitude. In both stack pairs of the *cis* and *trans* forms (Figs. 3(b) and 4(b)), the interplanar distance and the slip angles are 3.20 Å and 46°, respectively. So the stack pairs make the determinant contribution to the bathochromic shift. The resulting band due to intermolecular interactions is considered to be quite sensitive to molecular arrangement. Thus, a change in absorption maximum or intensity of the band is expected to appear when the molecular stack is disturbed, for example, by mechanical shears. The color change actually occurs in Pigment Black 31 from black to red. However, no color change is recognized in BIP. Whether the material is sensitive to mechanical shears or not, depends presumably on the density of the material. The densities of Pigment Black 31 are rather low (1.430 and 1.382 for phases I[12] and II[13], respectively; whereas BIP shows much higher densities: 1.551 and 1.602 for the *cis* and *trans* forms, respectively, as shown in Table 1.

Conclusions

The electronic structure of the *cis* and *trans* isomers of BIP has been investigated from the standpoint of the crystal structure and intermolecular interactions. The *cis* form gives an absorption band in solution at slightly longer wavelengths than the *trans* one, as borne out by MO calculations. This tendency is also the case in the solid state. In both isomers, two absorption bands appear in the visible region, covering the whole visible region (*i.e.* black color). The shorter-wavelength band is due to individual molecules and the longer-wavelength band arises from excitonic interactions between transition dipoles along molecular stack.

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Author Biography

Jin Mizuguchi obtained his B. Sc. in chemistry from Sophia University in 1970, Dr. of Science from the University of Tokyo in 1982 and Venia Docendi from the University of Bern in 1994. He worked 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.