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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 that exhibit a variety of shades from vivid red to black. We have focused on the title compound benzimidazo perylene (BIP) as a potential substitute for carbon black used widely as the black pigment in paint and imaging industries. In the present investigation, 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 of BIP is characterized by two absorption bands in the visible region in both isomers: the shorter-wavelength band is due to individual molecules and the longer-wavelength band appears as a result of excitonic interactions between transition dipoles. Especially, the interaction along the molecular stack is attributed to the appearance of the longer-wavelength band to cover the whole visible region together with the molecular band. BIP is also found to be quite insoluble in any organic solvents and extremely resistant to light and heat. © 2006 Society for Imaging Science and Technology.*
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INTRODUCTION

Carbon black (CB) is an excellent black pigment on the market used widely as the material 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 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 prepared directly on thin-film transistors. There is also a demand for a black pigment that is free from infrared (IR) absorption, because the pigment dispersed layers exposed to the sunshine in the open air accumulate heat, leading easily to the deterioration of polymers used as vehicles. For these reasons, an environmentally friendly, electrically insulating black pigment with no IR absorption is in demand.

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. At present, there are two commercial products (Pigment blacks 31 and 32 from BASF) based on the peryleneimide chromophore.[1] Pigment black 31 [*N*,*N*′-bis(2-phenylethyl)perylene-3,4:9,10-bis(dicarboximide)], for example, is characterized by two absorption bands in the visible region together with an absorption dip around 550 nm, yielding a shade of greenish-black. In addition, the color changes easily from black to red due to mechanical shearing.[2] We have previously carried out an in-depth study on the electronic structure of representative peryleneimide pigments from the standpoint of crystal structure as well as intermolecular interactions.[2–4] The conclusion of these investigations can be summarized as follows. The color in the solid state is mainly determined by two characteristic absorption bands in the visible region: the shorter wavelength band is due to individual molecules that appear in common in all perylene derivatives; whereas the longer wavelength band is caused by interactions between transition dipoles. Therefore, the color in the solid state can change, depending on the extent of exciton coupling on the basis of the molecular arrangement. The red color appears when the coupling is quite small; whereas the maroon and black colors are characterized by medium and strong exciton coupling, respectively.

On the basis of the earlier mechanism, we have mapped out a strategy in an attempt to achieve a real black pigment on the basis of peryleneimide compounds. In order to compensate the absorption dip around 520 nm in Pigment Black 31, it is necessary to use a larger perylene skeleton compared with the peryleneimide chromophore. This requirement is fulfilled by benzimidazo perylene derivatives [the title compound benzimidazo perylene[5–7] (BIP), Fig. 1] which shows a molecular absorption band around 600 nm. Then, we believed that the whole visible region could be covered by the molecular band together with an additional band due to excitonic interactions. In fact, BIP is found to satisfy these requirements. This article deals with the electronic structure of the *cis* and *trans* isomers of BIP on the basis of the crystal structure and intermolecular interactions.

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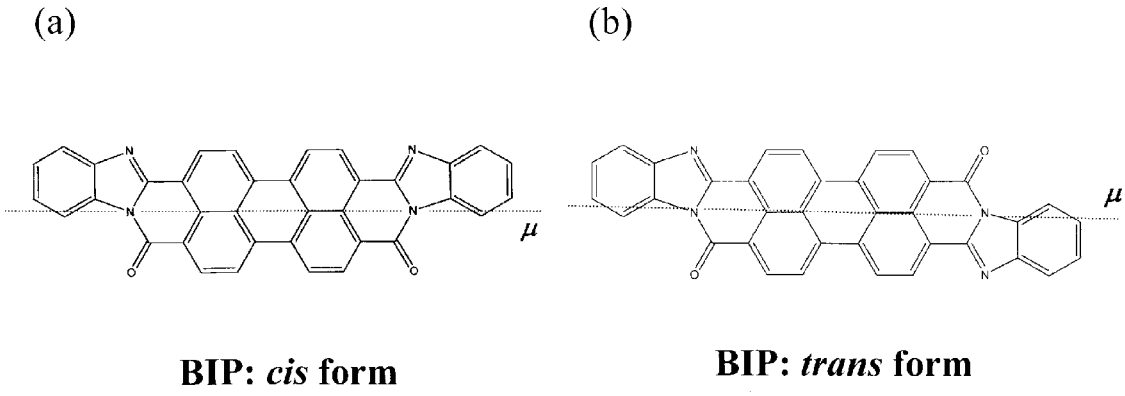


Figure 1. Molecular conformation of BIP: (a) *cis* form and (b) *trans* form. The direction of the transition dipole is designated by dotted lines.

EXPERIMENT

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

BIP was synthesized by the reaction of perylenetetracarboxylic dianhydride with 1,2-phenylenediamine in phenol at 483 K for 6 h.[7] 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. The *cis* or *trans* conformation has been confirmed by means of solution spectra together with molecular orbital calculations.

BIP powders of each form were purified twice by sublimation under argon at about 675 K, using a two zone furnace.[8] Single crystals were then grown from the vapor phase in a closed system at about 650 K. After 48 h, a number of needle-shaped crystals were obtained in both *cis* and *trans* compounds. The single crystals were used for structure analysis as well as for measurements of polarized reflection spectra.

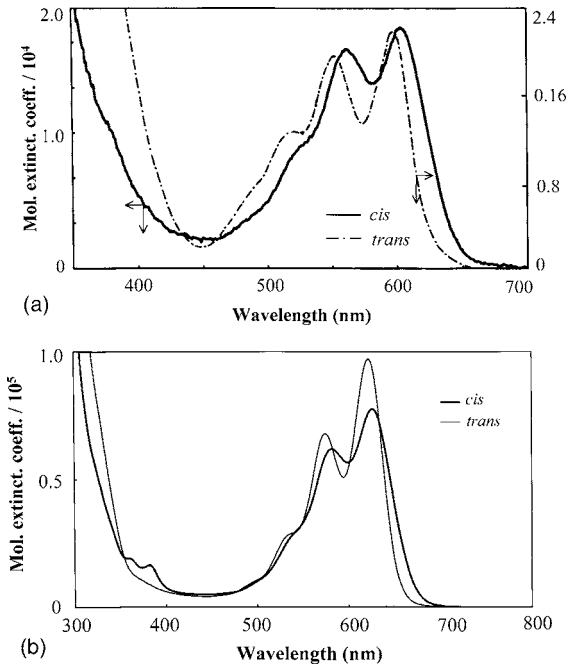


Figure 2. Solution spectra of the *cis* and *trans* forms: (a) in dimethylsulfoxide and (b) in *m*-cresol.

Measurements

Ultraviolet (UV) visible spectra were recorded on a UV-2400PC spectrophotometer (Shimadzu). Diffuse reflectance spectra for powders were measured on a UV-2400PC spectrophotometer in combination with an integrating sphere attachment (ISR-240A from Shimadzu). Measurements for polarized reflection spectra were made on single crystals by means of an UMSP 80 microscope-spectrophotometer (Carl Zeiss). 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 Calculations

The geometry of the *cis* and *trans* isomers of BIP molecules were optimized by means of the AM1 Hamiltonian of *MOPAC* program package.[9] The *INDO/S* program used for spectroscopic calculations is part of the *ZINDO* program package.[10]

RESULTS AND DISCUSSION

Solution Spectra

Figure 2(a) shows the solution spectra of the *cis* and *trans* isomers in dimethylsulfoxide (DMSO). [BIP is quite insoluble in DMSO (2 mg/1000 ml of DMSO.) The *trans* form is even less soluble in DMSO than the *cis* form.] The absorption maximum of the *cis* form is located at slightly longer wavelength than that of the *trans* one. This observation agrees with the results of molecular orbital (MO) calculations shown in Table I. Both spectra exhibit a typical progression of absorption bands starting from around 605 to 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 as 0-0, followed by the 0-1, 0-2, and 0-3 vibronic transitions as shown.

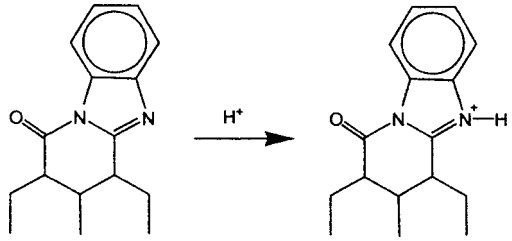
Figure 2(b) shows the absorption spectra of the *cis* and *trans* isomers in *m*-cresol. (BIP is by far more soluble by

Table I. Geometry optimization and optical absorption bands for the *cis* and *trans* forms.

	Geometry optimization	Optical absorption bands			
	Heat of formation (kcal/mol)	Calculated		Observed	
		λ(nm)	*f*	λ(nm)	log ε
Cis form: initial	192.2	485.2	1.75	606.5[a]	4.25
Mono-protonated	332.2	630.8	1.14	626.5[b]	4.88
di-protonated	512.9	671.2	0.69	···	···
Trans form: initial	192.1	481.7	1.84	603.0[a]	4.30
Mono-protonated	332.9	606.9	1.47	622.5[b]	4.99
di-protonated	513.3	621.7	1.01	···	···

[a]measured in DMSO

[b]measured in *m*-cresol



Protonation at the double bonded N atoms

several orders of magnitude in *m*-cresol due to protonation as compared with DMSO.) Here again, the absorption maximum of the *cis* form appears at longer wavelengths than that of the *trans* one. In addition, the absorption maximum occurs at longer wavelengths than that in DMSO. This is due to the protonation at the double-bonded N atoms of BIP shown in the inset of Table I, also as born out by MO calculations described later.

MO Calculations

Table I details the heat of formation of the optimized geometry as well as spectroscopic calculations for the *cis* and *trans* isomers for the initial and protonated states. The optimized geometry for the *cis* and *trans* forms are equally stable as shown by the heats of formation of 192.2 and 192.1 kcal/mol, respectively. Spectroscopic calculations also revealed that there is only one electronic transition in the visible region assigned to the highest occupied molecular orbital/lowest unoccupied molecular orbital π-π^* transition and that the absorption maximum of the *cis* isomer in the initial state appears at slightly longer wavelengths than that of the *trans* one. This tendency is also the case for the mono- and diprotonation at the double-bonded N atoms.

Structure Analysis

Table II lists 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

Table II. 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	$P2_{1/c}$	$P\bar{1}$
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 (deg)	—	89.35
β (deg)	99.21(1)	91.15(3)
γ (deg)	—	104.83(3)
Density (g/cm^3)	1.551	1.602

lattice is approximately half of the latter. The *cis* form crystallizes in space group of $P2_{1/c}$ while the *trans* one in $P\bar{1}$. The molecule has C_i symmetry in the *trans* form. On the other hand, the symmetry of the *cis* form is C_{2v}. This symmetry is obviously not compatible with space group $P2_{1/c}$, due to disorder of the atoms at the corners of the molecule.

The ORTEP plot of the *cis* and *trans* forms are shown in Figs. 3(a) and 3(b), respectively. Figures 4(a) and 4(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

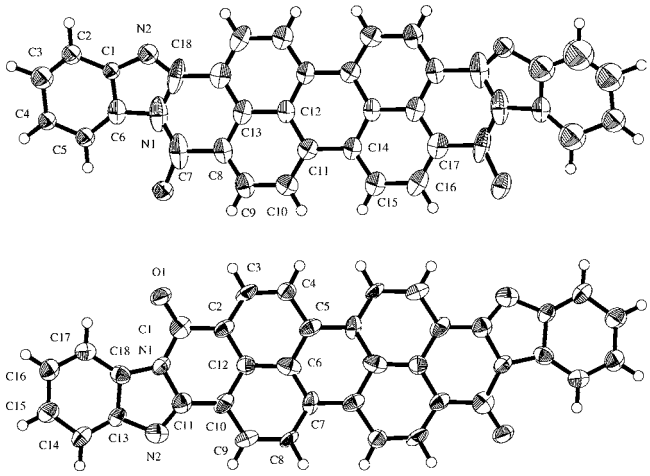


Figure 3. ORTEP plots: (a) *cis* form and (b) *trans* form.

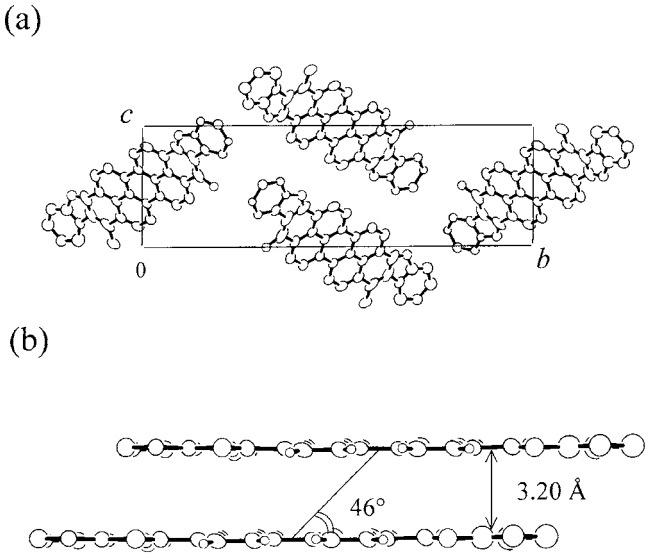


Figure 4. (a) Projection of the crystal structure of the *cis* form onto the (b,c) plane and overlap of two molecules.

the *trans* form onto the (b,c) plane and the overlap of two molecules are shown in Figs. 5(a) and 5(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.

Polarized Reflection Spectra Measured on Single Crystals

Figures 6(a) and 6(b) show the polarized reflection spectra of the *cis* form measured on the (a,c) plane of single crystals

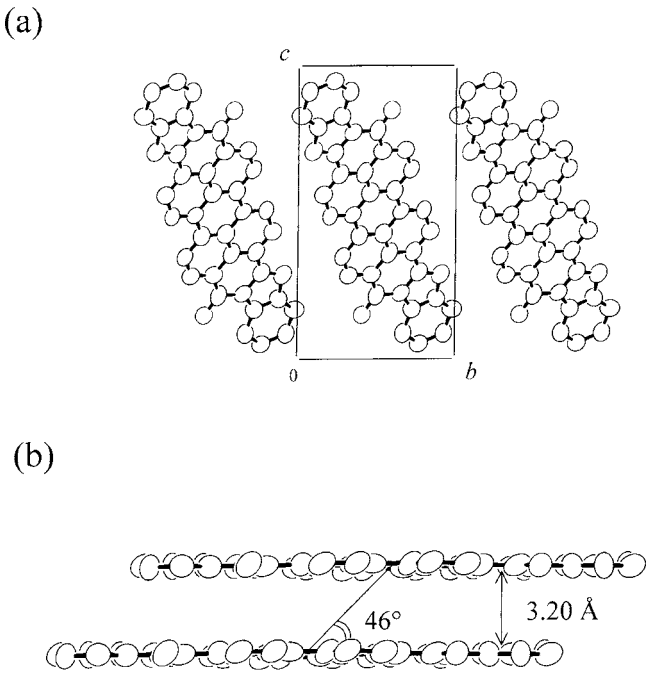


Figure 5. (a) Projection of the crystal structure of the *trans* form onto the (b,c) plane and overlap of two molecules.

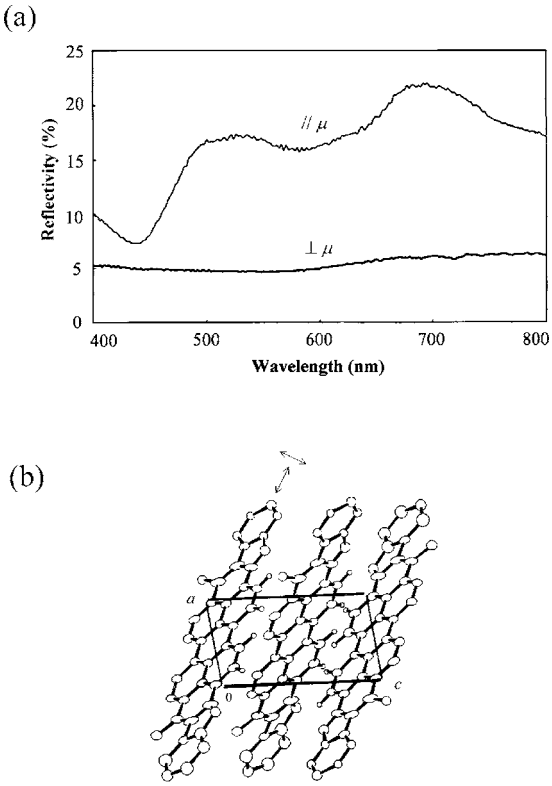


Figure 6. (a) Polarized reflection spectra of the *cis* form measured on the (a,c) plane of single crystals and (b) projection onto the (a,c) plane.

together with the corresponding projection. Polarized light was introduced 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. 6(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. 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;[2–4] 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[2–4] when an exciton coupling is involved in the optical process.

A similar spectroscopic behavior is also observed in polarized reflection spectra of the *trans* form as shown in Fig. 7. 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 the MO calculations (Table I).

Diffuse Reflectance Spectra Measured on Powders

Polarized reflection spectra shown earlier are typical of one extreme case of the whole spectra as measured by polarized

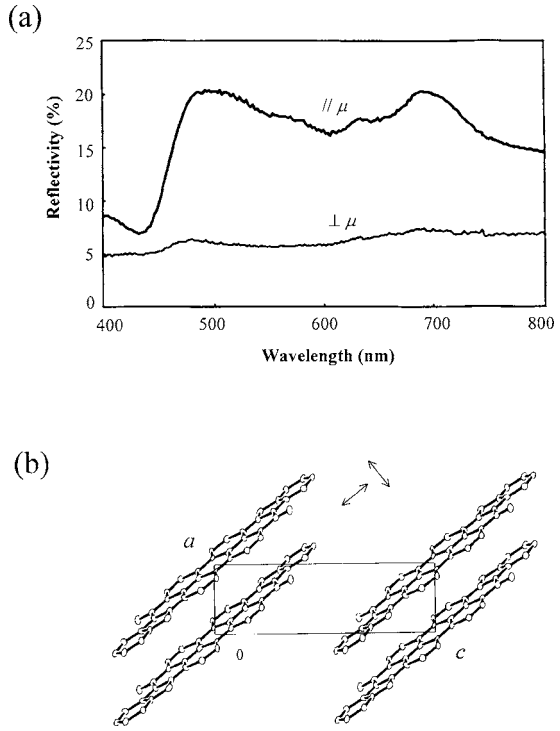


Figure 7. (a) Polarized reflection spectra of the *trans* form measured on the (a, c) plane of single crystals and (b) projection onto the (a, c) plane.

light on a specific crystal plane. Averaged information is given by diffuse reflectance spectra measured on powders.

Figure 8 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 9 is the diffuse reflectance spectrum of the powdered sample as synthesized without separation of two isomers.

Powders of the *cis* and *trans* forms are found to be quite insoluble in normal organic solvents. These are also extremely light and heat stable. No degradation was revealed on UV irradiation for a week as well as on heat treatment at 500 °C for several hours.

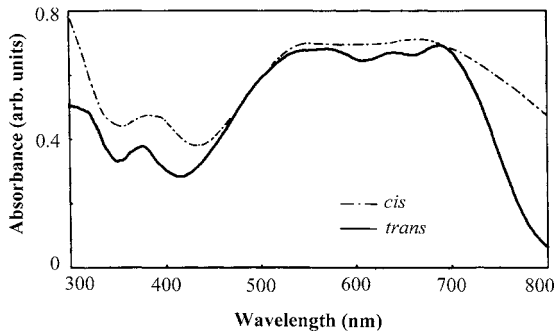


Figure 8. Diffuse reflectance spectra of the *cis* and *trans* forms.

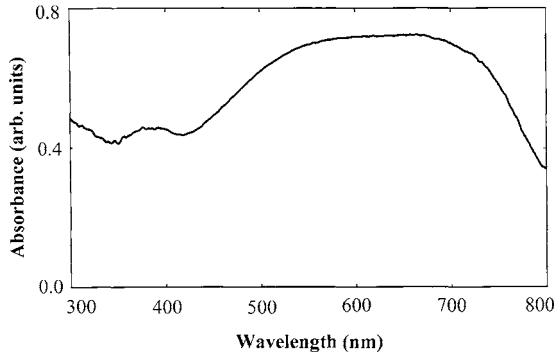


Figure 9. Diffuse reflectance spectrum of powders as synthesized without separation of two isomers.

Excitonic Interactions between Stack Pairs

We have pointed out in our previous investigations[2–4] the importance of the excitonic interactions in pigments, in which the absorption coefficient of the component molecule is quite large. The interaction energy ($\Delta E_{\text{exciton}}$) is given by the dipole-dipole equation:[11,12] $\Delta E_{\text{exciton}} = |\mu|^2(1-3\cos^2\theta)/r^3$, where the transition dipole is denoted by μ, the distance and angle between two transition dipoles by r and θ, respectively. As evident from the present equation, the overall energy shift is determined by the strength of the interneighbor coupling ($|\mu|^2$) which directly depends on the absorption coefficient of the molecule as well as on the mutual relative orientation of the transition dipoles in molecular assemblies. That is, the term $(1-3\cos^2\theta)/r^3$ determines the geometrical relationship of transition dipoles correlated with the crystal structure. Since this term falls off as the inverse cube of distance, most of the interaction would come from the nearest neighbors. The bathochromic or hypsochromic shift depends on the critical angle of $\theta = 54.7°$, below which the former will result and above which the latter will be the case.

We examine here the extent of the exciton coupling for molecule pairs in the lattice. Table III shows the spectral displacement due to excitonic interactions caused by the nearest neighbor molecules for the *cis* and *trans* forms. The transition dipoles are calculated by the INDO/S Hamiltonian using the x, y, z coordinate set of the x-ray structure analysis. The site of the molecules is designated by the fractional coordinates. The displacement energy is denoted by ΔE, and the minus and plus signs of the energy correspond to bathochromic and hypsochromic shifts, respectively. As judged from the geometrical term $(1-3\cos^2\theta)/r^3$ for the nearest molecule pairs on the molecular plane [Figs. 4(a) and 5(a)] as well as along the stacking axis [Figs. 4(b) and 5(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. In both stack pairs of the *cis* and *trans* forms [Figs. 4(b) and 5(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 spectral displacement due to excitonic splitting is considered to be quite sensitive to molecular arrangement

Table III. Nearest neighbors around the molecule at (a) (1/2.1/2,0) and (b) (1/2,1/2,1/2) and their displacement energies in BIP of the (a) *cis* and (b) *trans* form.

	Type of molecule pairs	Number of molecules	Site in fractional coordinates	r(Å)	θ (deg)	ΔE(cm^{-1})[a]
(a)	Stack pair	2	(0,1/2,0)	4.75	36.8	−6822
	Diagonal 1	2	(0,1/2,1)	10.58	84.1	647
	2	2	(1/2,1/2,1)	8.73	60.6	331
	3	2	(1,1/2,1)	9.25	54.6	−9
	4	2	(0,3/2,0)	28.5	41.8	−23
	5	2	(1/2,3/2,0)	28.1	50.1	−8
	6	2	(1,3/2,0)	28.5	58.7	7
	7	2	(0,3/2,1)	30.0	50.5	−6
	8	2	(1/2,3/2,1)	29.4	57.4	4
	9	2	(1,3/2,1)	2906	64.7	14
			μ(Å)=2.614			
(b)	Stack pair	2	(3/2,1/2,1/2)	4.7	46.6	−3121
	Diagonal 1	2	(1/2,−1/2,1/2)	8.3	68.1	807
	2	2	(1/2,1/2,3/2)	14.7	47.1	−97
	3	2	(1/2,−1/2,3/2)	16.8	38.7	−137
	4	2	(1/2,3/2,3/2)	17.0	65.9	80
	5	2	(−1/2,−1/2,1/2)	10.5	53.0	−59
	6	2	(3/2,−1/2,1/2)	8.4	88.9	1312
	7	2	(−1/2,1/2,3/2)	15.4	30.3	−268
	8	2	(3/2,1/2,3/2)	15.5	64.2	90
	9	2	(−1/2,−1/2,3/2)	17.9	24.2	−204
	10	2	(3/2,−1/2,3/2)	17.0	54.4	−3
	11	2	(−1/2,3/2,3/2)	17.0	53.1	−13
	12	2	(3/2,3/2,3/2)	18.2	78.3	114
			μ(Å)=2.605			

[a]The minus and plus signs denote bathochromic and hypsochromic shifts, respectively.

because of the geometrical term of the interaction energy. 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 shear. The color change actually occurs in Pigment Blacks 31 and 32 from black to red, as described in the Introduction. However, no color change is recognized in BIP. Whether the material is sensitive to mechanical shear or not depends largely on the density of the material. The density of Pigment Blacks 31 is rather low: 1.430 and 1.382 for phases I (Ref. 13) and II,[14] respectively. On the other hand, BIP possesses a much higher density as shown in Table II: 1.551 and 1.602 for the *cis* and *trans* forms, respectively.

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, with a potential application to black pigment in mind. The *cis* and *trans* forms are found to crystallize in space groups $P2_{1/c}$ and $P\bar{1}$, respectively. Although the *b* lattice of the *cis* form is twice as long as that of the *trans* one, other crystal parameters are

quite similar, particularly the molecular overlap. In both isomers, two absorption bands appear in the visible region and cover 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 the molecular stack. BIP is also found to be quite insoluble in normal organic solvents and extremely light and heat stable.

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