

Electronic Structure of Thiazine-Indigo Pigment on the Basis of the Crystal Structure

Takatoshi Senju* and Jin Mizuguchi

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, 240-8501 Yokohama, Japan

Received: January 5, 2005; In Final Form: February 23, 2005

Thiazine-indigos are novel hydrogen-bonded pigments developed recently by Clariant that exhibit a variety of shades from yellow to red. Among these, a commercially available chlorinated derivative (THI) gives a color of vivid red, although it is only pale yellow in solution. For this reason, electronic characterization of THI has been carried out on the basis of the crystal structure. There are chains of intermolecular hydrogen bonds between the N–H group of one molecule and the O atom of the neighboring one along the *b*-axis, forming a two-dimensional hydrogen bond network. The direction of the transition dipole points along the long molecular axis, and the transition dipoles are arranged in “head-to-tail” fashion along the (*b*,*−c*) diagonal direction. The large bathochromic shift upon crystallization can be mostly attributed to excitonic interactions between transition dipoles arranged diagonally along the stacking axis as well as those in head-to-tail fashion on the molecular plane.

1. Introduction

In organic pigments, there is a class called hydrogen-bonded pigments as represented by indigos, quinacridones (QA), and diketopyrrolopyrroles (DPP).¹ Thiazine-indigos are novel hydrogen-bonded pigments developed recently by Clariant that cover a variety of shades from yellow to red, depending on the substituent.² Among these, a commercially available chlorinated derivative (Pigment Red 279 abbreviated to THI: Figure 1) gives a color of vivid red. THI features a new chromophoric system similar to that of indigo or thioindigo. There are also two pairs of N–H and C=O groups necessary for the formation of N–H···O intermolecular hydrogen bonds, as found in QA and DPP.¹ As is well-known, indigo and thioindigo are deeply colored in solution, while THI appears only pale yellow. However, in the solid state, THI exhibits a vivid red color, indicating a large bathochromic shift upon crystallization. For this reason, we have previously carried out structure analysis on single crystals of THI as a step for the electronic characterization.³ THI is found to crystallize in space group $P\bar{1}$ with $Z = 1$. The molecule is entirely planar, characterized by C_i symmetry. There are chains of intermolecular N–H···O hydrogen bonds between the N–H group of one molecule and the O atom of the neighboring one on the molecular plane, forming a two-dimensional network of hydrogen bonds.

The present investigation aims at elucidating the color generation mechanism of THI in the solid state from the standpoint of intermolecular interactions on the basis of the crystal structure. Special attention is paid to the direction of the transition dipole and its geometrical arrangement, both of which are crucial for the discussion of excitonic interactions in the solid state. We also discuss similarity and nonsimilarity in the electronic structure of THI to those of indigos, quinacridones, and diketopyrrolopyrroles.

2. Experimental Section

THI was obtained from Clariant and purified twice by sublimation, using a two-zone furnace.⁴ Single crystals were

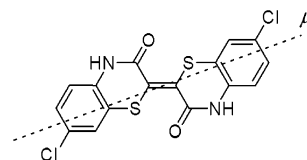


Figure 1. Molecular conformation of chlorinated thiazine-indigo (THI). The direction of the transition dipole (μ) as deduced from MO calculations is designated by the dotted line.

then grown from solution in dimethyl sulfoxide (DMSO) using an autoclave. The evaporated thin films were prepared on glass substrates using a Tokyo Vacuum EG-240 under high vacuum. The evaporated films were exposed to acetone vapor for several hours to bring about the rearrangement of molecules. X-ray diffraction diagrams of evaporated THI were measured with a Rigaku RINT 2000.

Vapor treatment is considered to loosen the crystal lattice so that the molecules can slide and/or rotate to find energetically more stable sites. In this way, we can enhance the crystallization of evaporated films which are not always well-crystallized as evaporated and often oriented, depending on the substrate used.

UV–vis spectra were recorded on a Shimadzu UV-2400PC spectrophotometer. Polarized reflection spectra were measured on single crystals by means of a Carl Zeiss UMSP 80 microscope–spectrophotometer. Semiempirical molecular orbital (MO) calculations were made for THI using *Quantum CAChe*, version 3.2.⁵ Geometry was optimized by the AMI Hamiltonian,⁶ and absorption bands were then calculated on the basis of the INDO/S Hamiltonian.⁷

3. Results and Discussion

3.1. Crystal Structure.³ The crystal system is triclinic and the space group is $P\bar{1}$. The lattice parameters are as follows: $a = 4.5934(6)$, $b = 7.8303(8)$, $c = 10.403(1)$ Å, $\alpha = 92.040(9)$, $\beta = 99.38(1)$, $\gamma = 94.19(1)^\circ$. Figure 2a,b shows the projection of the crystal structure onto the (*b*,*c*) plane and the molecular arrangement along the stacking axis, respectively. On the molecular plane, there are chains of intermolecular hydrogen

* To whom correspondence should be addressed. Phone/Fax: +81 45 339 4320. E-mail: tsenju@ynu.ac.jp.

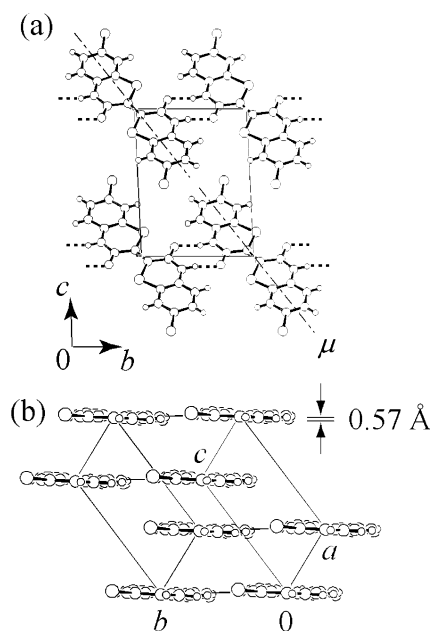


Figure 2. Molecular arrangement: (a) projection of the crystal structure onto the (b,c) plane and (b) molecular stack. The dotted lines denote intermolecular N—H...O hydrogen bonds, while the dashed lines designate the direction of the transition dipole (μ). There is a small step of about 0.57 Å between two hydrogen-bonded molecules.

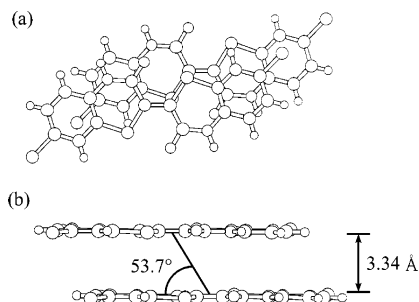


Figure 3. Overlap of two molecules along the stacking a -axis: as seen (a) from the top and (b) from the side.

bonds along the b -axis between the N—H group of one molecule and the O atom of the neighboring one. The present N—H...O hydrogen bonds form a two-dimensional hydrogen bond network as found in diketopyrrolopyrroles⁸ and 2,9-dimethylquinacridone.⁹ The N/O distance and the NH/O angle are 2.832 Å and 170°, respectively. It is interesting to note that there is a small step of about 0.57 Å between two molecules on the molecular plane (Figure 2). The present step between two hydrogen-bonded molecules is rather unusual for hydrogen-bonded pigments. Other examples are also found in 2,9-dimethylquinacridone⁹ as well as modifications I and II of dithioketopyrrolopyrroles.^{10,11}

Figure 3 shows the overlap of two molecules along the stacking axis.

3.2. MO Calculations and Solution Spectrum. Geometry optimization gives an entirely flat molecule of THI. Spectroscopic calculations revealed that the longest-wavelength band appears around 386.9 nm with oscillator strength of 0.73. The present band is due to the HOMO/LUMO π — π^* electronic transition whose transition dipole points along the long molecular axis as shown in Figure 1. This is the only electronic transition which is expected to appear in the visible region.

Figure 4 shows the solution spectrum of THI in DMSO. A progression of the absorption bands is observed, which starts from 480 nm toward shorter wavelengths. Because these bands are equally spaced (about 1700 cm^{-1}) and the MO calculations

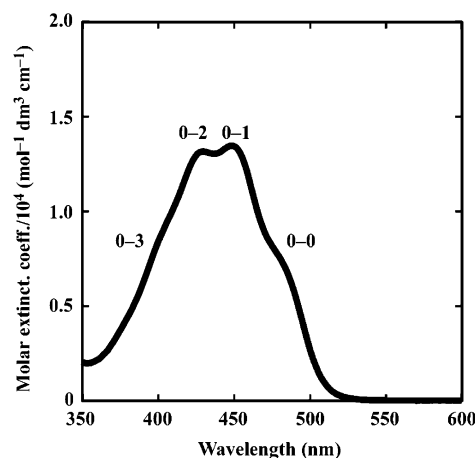


Figure 4. Solution spectrum of THI in DMSO.

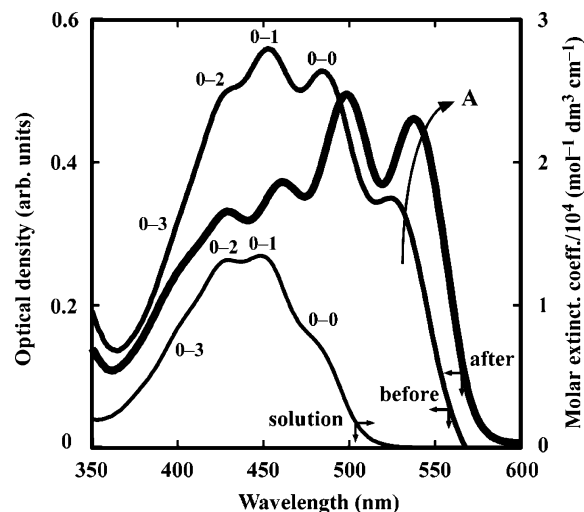


Figure 5. Solid-state spectra of evaporated THI before and after vapor treatment (film thickness: ca. 1000 Å), together with the solution spectrum.

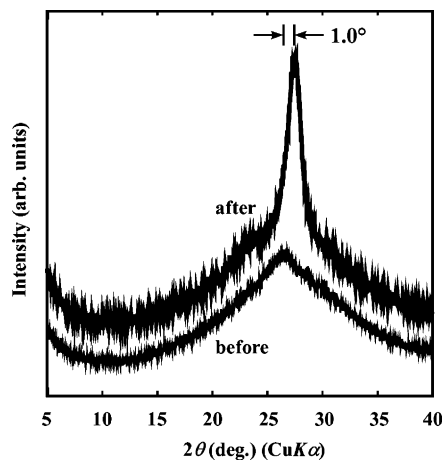
predict only one electronic transition in the visible region, the longest-wavelength shoulder around 480 nm is assigned to the pure electronic band which corresponds to the HOMO/LUMO π — π^* transition and is denoted by the 0—0 transition. The subsequent bands around 450, 430, and 400 nm are vibronic transitions (i.e., vibrational—electronic transition) as attributed to the 0—1, 0—2, and 0—3 transitions, respectively. The same tendency is also observed in other solvents such as 1,4-dioxane, *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), and 2-pyrrolidone. However, the extent of the bathochromic shifts is slightly different: 5 nm in DMF and 10 nm in DMSO, NMP, and 2-pyrrolidone relative to the solution in dioxane, respectively. The present spectral shift follows the relative order of increasing polarity of the solvents. This is due to the formation of intermolecular hydrogen bonds between the NH group (donor) of THI and the O atom (acceptor) of the solvent, as described in our previous reports on hydrogen-bonded pigments.^{12,13}

3.3. Solid-state Spectra and X-ray Diffraction Diagrams in Evaporated Films. Figure 5 shows the solid-state spectra of evaporated THI before and after vapor treatment, together with the solution spectrum in DMSO. The spectral shape of evaporated THI before vapor treatment is quite similar to that in solution. However, one additional band designated by band A is recognized around 524 nm. Then, except for band A, one-to-one correspondence of the absorption bands is possible

TABLE 1: Geometry of the Nearest Neighbors around the Molecule at (0,0,0) and Their Displacement Energies

type of molecule pairs	no. of equivalent molecules	site (fractional coordinates)	<i>r</i> (Å)	θ (°)	ΔE (cm ⁻¹) ^{a,b}
hydrogen bond pair	2	(0,1,0)	7.83	63.2	245
head-to-tail pair	2	(-2,-1,1)	16.744	1.9	-128
stack pair	2	(1,0,0)	4.593	53.7	-164
diagonal pair I	2	(1,1,0)	8.784	44.6	-230
diagonal pair II	2	(-1,0,1)	12.037	29.4	-220
diagonal pair III	2	(-1,-1,1)	14.379	12.9	-187
diagonal pair IV	2	(1,-1,0)	9.363	85.0	358

^a μ (Å) = 1.612. ^b The plus or minus sign denotes hypsochromic or bathochromic shift, respectively.

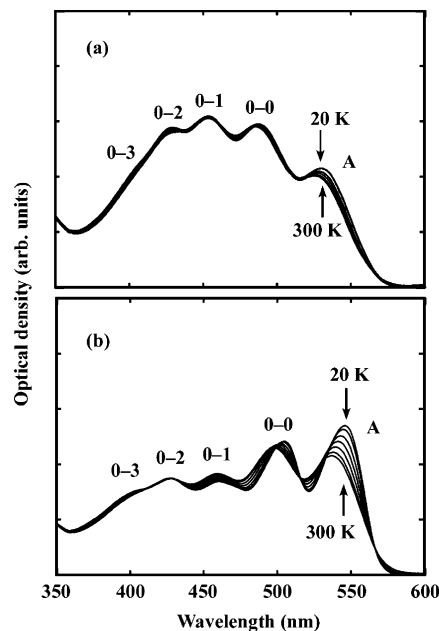
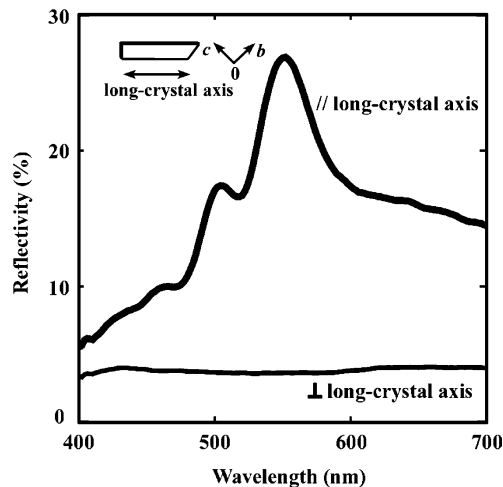
**Figure 6.** X-ray diffraction diagrams of evaporated THI before and after vapor treatment.

between the solution and solid-state spectra. This evidently indicates that band A is a new band which appears upon crystallization and is due to intermolecular interactions. In addition, band A is further displaced toward longer wavelengths and intensified because of vapor treatment. The present spectral change is well-correlated with molecular rearrangement as shown by X-ray diffraction analysis described below.

Figure 6 shows the X-ray diffraction diagrams of evaporated THI before and after vapor treatment. The broad diffraction band around $2\theta = 26.3^\circ$ is due to the glass substrate used. The halo diffraction diagram before vapor treatment is rather indicative of an amorphous phase, although the N—H···O hydrogen bond network is present in this state as shown by IR spectra (not shown here). Then, vapor treatment induces crystallization as shown by the diffraction peak around $2\theta = 27.3^\circ$ ($d = 3.26$ Å). The present d -value agrees approximately with the interplanar distance of the stacked molecules in single crystals,³ indicating that the molecules are ordered along the stacking axis because of vapor treatment.

3.4. Temperature Dependence of Absorption Spectra in Evaporated Films. The temperature dependence of the absorption spectra often serves as a good measure for the involvement of intermolecular interactions in the optical absorption. At low temperatures, the crystal lattice is significantly contracted to enhance intermolecular interactions. Therefore, the absorption band due to intermolecular interactions is expected to exhibit appreciable temperature dependence at low temperatures.

Figure 7a,b shows the temperature dependence of the absorption spectra of evaporated THI before and after vapor treatment, measured in the temperature range between 20 and 300 K. Before vapor treatment, band A shows insignificant but still more temperature dependence as compared with that of the 0-0, 0-1, 0-2, and 0-3 bands. Then, vapor treatment brings about the significant temperature dependence of band A. This clearly indicates that the enhanced intermolecular interaction due to

**Figure 7.** Temperature dependence of absorption spectra of evaporated THI before and after vapor treatment: (a) before and (b) after.**Figure 8.** Polarized reflection spectra for THI measured on the (100) plane (see Figure 2a for the corresponding projection). The direction of the transition dipole (μ) is shown in Figure 1.

the ordering of the molecules along the stacking axis is directly responsible for the appearance of the longest-wavelength band. Then, an important question arises as to the origin of intermolecular interactions involved in band A. We will discuss this point later in section 3.6.

3.5. Polarized Reflection Spectra Measured on Single Crystals. Figure 8 shows the polarized reflection spectra measured on the (100) plane of THI single crystals. The projection of the crystal structure onto the (b,c) plane is shown

in Figure 2a, while the direction of the transition dipole (μ) is presented in Figure 1. It is important to note that the transition dipoles are aligned along the $(b,-c)$ diagonal direction in a nearly head-to-tail fashion.

An intense reflection band appears at about 550 nm, accompanied by two small bands around 500 and 470 nm for polarization parallel to the long crystal axis (i.e., $(b,-c)$ diagonal direction). On the other hand, these bands are completely quenched for polarization perpendicular to the long crystal axis. The appearance and disappearance of all reflection bands for different polarizations indicate clearly that there is only one type of electronic transition in the visible region and that the direction of the transition dipole points along the long molecular axis. This is in good agreement with the result of the MO calculations described in section 3.2. The reflection spectrum for polarization parallel to the long crystal axis is in accord with the absorption spectrum of evaporated THI after vapor treatment (Figure 5), especially with the spectrum at 20 K shown in Figure 7b.

3.6. Excitonic Interactions and the Origin of the Longest-Wavelength Band. The excitonic interactions¹⁴ play an important role in dyestuffs and pigments, where the component molecule has a large absorption coefficient proportional to the square of the transition dipole. The interaction energy ($\Delta E_{\text{exciton}}$) is given by the dipole–dipole equation: $\Delta E_{\text{exciton}} = |\mu|^2(1 - 3 \cos^2 \theta)/r^3$, where the transition dipole is denoted by μ and the distance and angle between two transition dipoles by r and θ , respectively. As evident from the present equation, the overall shift energy is determined by the strength of the interneighbor coupling ($|\mu|^2$) 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. Because 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 $\theta = 54.7^\circ$ (i.e., $\Delta E = 0$), below which the former will result and above which the latter will be the case. The maximum bathochromic shift arises when the transition dipoles are arranged in a head-to-tail fashion: that is, two transition dipoles are aligned as shown in Figure 2a.

Because the molar extinction coefficient of THI is very large (about 13 400 as shown in Figure 4), it is highly probable that the excitonic interactions between transition dipoles prevail in THI and cause spectral shifts to occur. Table 1 summarizes the major contributions of the nearest neighbors to the spectral shift as evaluated by the dipole–dipole equation. Judging from the distance (r) and angle (θ) in Table 1, it is apparent that the largest contribution is made by diagonal pairs I and II, followed by diagonal pair III, stack, and head-to-tail pairs. The hypsochromic shifts are induced by diagonal pair IV and the H-bond pair. The summation over all bathochromic shifts exceeds the hypsochromic contribution by an amount of about 1435 cm^{-1} .

Similar bathochromic displacements due to excitonic interactions are observed in organic pigments, for example, in diketopyrrolopyrroles¹⁵ and dicarboxyimide perylenes.¹⁶

3.7. Similarity and Nonsimilarity in Electronic Structure of THI to those of Indigo, Quinacridone, and Diketopyrrolopyrrole. THI is a newcomer in hydrogen-bonded pigments, which include indigo, QA, and DPP. These pigments are characterized by intermolecular hydrogen bonds between the N–H group of one molecule and the O atom of the neighboring one.

Indigo is different from QA and DPP in the direction of the transition dipole as well as the geometrical arrangement of

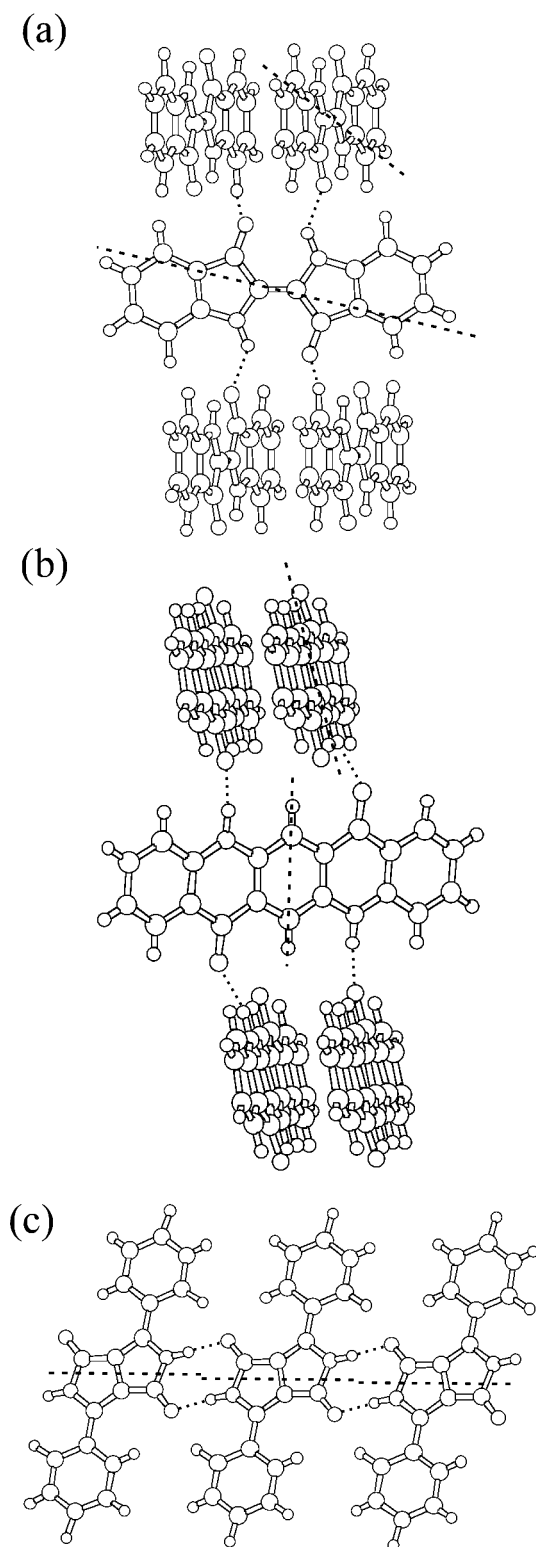


Figure 9. Molecular conformation and the direction of the transition dipole: (a) indigo, (b) QA, and (c) DPP. In QA and DPP, the transition dipoles are aligned by intermolecular hydrogen bonds, whereas the intermolecular hydrogen bonds in indigo are formed irrespective of the direction of the transition dipole.

transition dipoles as shown in Figure 9.¹⁷ Figure 9 illustrates the molecular arrangement together with the direction of the transition dipole for indigo, QA, and DPP. The transition dipole in QA and DPP lies perpendicular to the long molecular axis; in other words, along the direction of the N–H \cdots O hydrogen bond. On the contrary, the transition dipole of indigo points along the long molecular axis. In QA and DPP, the color in

solution is pale yellow, while it is vivid red in the solid state. On the other hand, indigo is deeply colored (i.e., blue) even in solution, whereas no further significant change in color takes place upon crystallization. The present situation can be well-interpreted in terms of the geometrical arrangement of the transition dipoles. QA and DPP bear a color of pale yellow in solution, because the transition dipole is perpendicular to the long molecular axis. However, a large bathochromic shift occurs on going from the solution to the solid state because of intermolecular interactions between transition dipoles arranged in a head-to-tail fashion (Figure 9b,c). On the contrary, indigo is deeply colored blue in solution, because the transition dipole lies along the long molecular axis (Figure 9a). However, no further appreciable bathochromic displacement is the case in indigo, because the transition dipoles are not aligned in a head-to-tail fashion.

In the case of THI, the situation is quite similar to that of indigo as far as the direction of the transition dipole is concerned (Figure 1). On the other hand, THI resembles QA and DPP in spectroscopic behavior, showing a yellowish color in solution and a large bathochromic displacement upon crystallization. The present large bathochromic shift is caused by excitonic interactions between diagonal pairs as well as a head-to-tail one, as described in the previous section. Especially, the head-to-tail arrangement in THI is formed quite irrespective of the hydrogen bond. The present, accidental head-to-tail arrangement reflects the striking difference in spectroscopic behavior between THI and indigo. In summary, THI is quite similar in molecular structure to indigo, but it more closely resembles QA and DPP in the spectroscopic sense.

4. Conclusions

Electronic structure has been investigated on the basis of the crystal structure. The large bathochromic shift upon crystallization can be mostly attributed to interactions between transition dipoles arranged diagonally along the stacking axis as well as those arranged in a head-to-tail fashion on the molecular plane. The present head-to-tail arrangement, irrespective of the hydrogen bond, is rather accidental and typical of THI. THI is quite similar in molecular structure to indigo, but

it more closely resembles QA and DPP in the spectroscopic sense. The present conclusion opens up a new horizon regarding the design of a variety of colors by incorporating intermolecular interactions.

Acknowledgment. We thank Clariant for providing the sample of THI. T.S. thanks the Ministry of Education, Culture, Sports, Science and Technology, Japan for financial support (Grant-in-Aid for Young Scientists (B) 16750159).

References and Notes

- (1) Herbst, W.; Hunger, K. *Industrial Organic Pigments: Production, Properties, Applications*, 3rd ed.; VCH: Weinheim, 2004.
- (2) (a) Kaul, B. L.; Piastra, B. Thiazine indigo pigments, their preparation, their solid solutions and their application. PCT International Application WO 9832800, 1998. (b) Kaul, B.; Piastra, B.; Borchert, T. Thiazine-indigo pigments for coloration of warp-free polyolefins. European Patent Application EP 1076076, 2001. (c) Rothe, P.; Unverdorben, L.; Piastra, B. Production of trans-thiazine-indigo pigments. European Patent Application EP 1167459, 2002. (d) Clariant International, Ltd. Pigment formulation and their production. European Patent Application EP 1416018, 2004.
- (3) Senju, T.; Mizuguchi, J. Z. *Kristallogr. — New Cryst. Struct.* **2003**, 218, 129.
- (4) Mizuguchi, J. *Cryst. Res. Technol.* **1981**, 16, 695.
- (5) *Quantum CAChe*, version 3.2; Fujitsu, Ltd.: Tokyo, Japan.
- (6) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, 107, 3902.
- (7) Kotzian, M.; Rosch, N.; Zerner, M. C. *Theor. Chim. Acta* **1992**, 81, 201.
- (8) Mizuguchi, J.; Grubenmann, A.; Wooden, G.; Rihs, G. *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, B48, 696.
- (9) Mizuguchi, J.; Senju, T.; Sakai, M. Z. *Kristallogr. — New Cryst. Struct.* **2002**, 217, 525.
- (10) Mizuguchi, J.; Rochat, A. C.; Rihs, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, C46, 1899.
- (11) Mizuguchi, J.; Arita, M.; Rihs, G. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, C47, 1952.
- (12) Mizuguchi, J.; Rochat, A. C.; Rihs, G. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, 98, 19–28.
- (13) Mizuguchi, J. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, 98, 28–34.
- (14) Kasha, M. Molecular Excitons in Small Aggregates. In *NATO Advanced Study Institute Series, Series B*; Bartolo, B. D., Ed.; Plenum Press: New York, 1976; Vol. 12, pp 337–363.
- (15) Mizuguchi, J. *J. Phys. Chem. A* **2000**, 104, 1817.
- (16) Mizuguchi, J.; Tojo, K. *J. Phys. Chem. B* **2002**, 106, 767.
- (17) Mizuguchi, J.; Endo, A.; Matsumoto, S. *J. Imag. Soc. Jpn. (Nippon Gazo Gakkaishi)* **2000**, 39, 94.