Electronic and Structural Characterization of a Piezochromic Indigoid: 11-(3′-Oxodihydrobenzothiophen-2′-ylidene)cyclopenta[1,2-b:4,3-b′]dibenzothiophene

J. Mizuguchi,* N. Tanifuji,[†] and K. Kobayashi[†]

Department of Applied Physics, Graduate School of Engineering, Yokohama National University, 240-8501 Yokohama, Japan

The title compound, a novel thioindigoid, undergoes a color change in the solid state from red to black due to mechanical shearing ("piezochromism"), and the color is also recovered either by heat or solvent treatment. The mechanism of the piezochromic effect has been studied in the present investigation on the basis of the crystal structure and thermal analysis. The absorption band in the initial red state is found to be similar to the one in solution, indicating that the molecular nature is well preserved even in the solid state. The color change (red → black) is then induced by mechanical shearing, accompanied by an additional, new band around 750 nm. The new band covers the whole visible region together with the band in the red phase to make the color black. The new band has been interpreted as arising from excitonic interactions between transition dipoles based on the re-organized molecular arrangement caused by mechanical shearing.

1. Introduction

The title compound, 11-(3′-oxodihydrobenzothiophen-2′-ylidene)cyclopenta-[1,2-b:4,3-b′]dibenzothiophene (abbreviated to OBCB, Figure 1), is a novel thioindigoid based on the indigo skeleton. OBCB has been synthesized in a series of our investigations on the solid-state reactions induced by charge-transfer interactions.[1,2] Interesting to say, OBCB is found to undergo a color change from red to black when the powders were ground in a mortar with a pestle. The present effect is called "tribo- or piezochromism". It is also of interest to note that the color is recovered when heated at about 280 °C for 2 h or immersed in organic solvents for several minutes. In this connection, the present investigation has been carried out to elucidate the color generation mechanism on the basis of the crystal structure and thermal measurements.

The piezochromism is defined as the color change due to mechanical stress imposed on a material. In the case of the piezochromism in organic compounds, there are two possible mechanisms. One is the color change occurring on the molecular basis. This is due to the change in molecular conformation caused by mechanical stress. The other involves changes in intermolecular interactions in the solid state that induce spectral shifts or cause a new band to appear. Because the OBCB is a rigid and entirely flat molecule as shown by structure analysis, it is highly probable that the color change occurs due to molecular rearrangement caused by mechanical stress rather than the change in molecular conformation. Therefore, we focus on the elucidation of the piezochromism of OBCB with particular emphasis on the characterization of a new absorption band around 750 nm that appears as a result of mechanical grinding.

2. Experimental Section

2.1. Sample preparation. OBCB was prepared by solid-state co-grinding of 11-(2-benzo[b]thienyl)cyclopenta[1,2-b:4,3-b′]-

* Corresponding author. E-mail: mizu-j@ynu.ac.jp.
† Current address: Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, 153-8902 Tokyo, Japan.
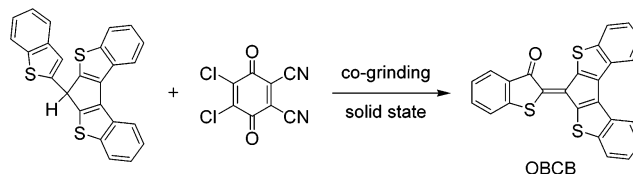

Figure 1. Preparation of OBCB by a solid-state reaction.

dibenzothiophene with dichlorodicyanobenzoquinone[1] as shown in Figure 1. The product was then purified by sublimation at about 340 °C, using a two-zone furnace.[3] The powdered sample was dark-red.

The single crystals were grown from the vapor phase in a closed system. After 48 h, a number of needle crystals were obtained. The single crystals were used for structure analysis[4] as well as for measurements of polarized reflection spectra.

2.2. Measurements. UV−Vis solution as well as diffuse reflectance spectra were recorded on a JASCO Ubest V-560 and V-570 spectrophotometer, respectively. The diffuse reflectance spectra on powders were corrected by the Kubelka−Munk equation. Powder X-ray diffraction diagrams were measured by a RAD-C diffractometer from RIGAKU. Measurements for polarized reflection spectra were made on single crystals by means of a 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. Heat flow was measured under nitrogen as a function of temperature by means of a differential scanning calorimeter (DSC, Thermo Plus DSC8230) from RIGAKU Ltd. The heating rate was 10 °C per min.

2.3. Molecular Orbital Calculations. Geometry of OBCB molecule was optimized by means of the AM1 Hamiltonian of MOPAC93.[5] The dipole moment (μ_D) calculated on the basis of the optimized geometry is shown in the form of a broken line in Figure 2. The spectroscopic calculations were then carried out on the optimized geometry using the INDO/S Hamiltonian in ZINDO program package.[6]
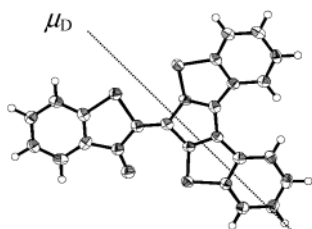
Figure 2. ORTEP plot of OBCB together with the direction of the dipole moment (μ_D).
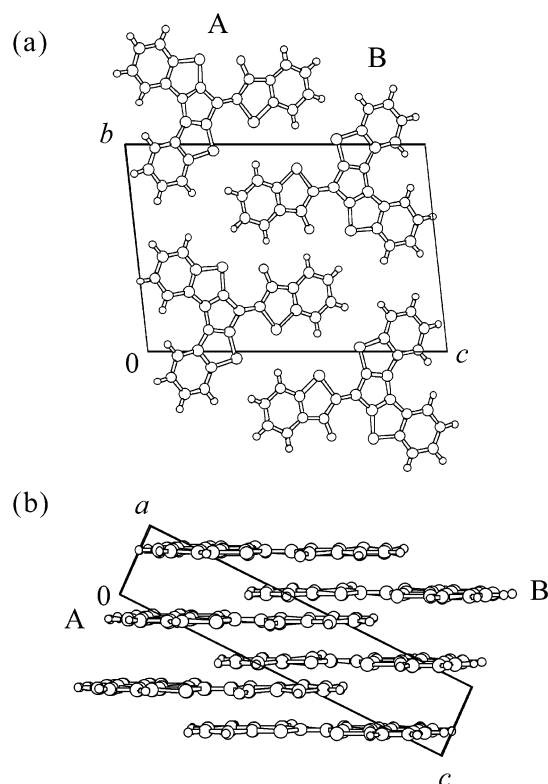

Figure 3. Molecular arrangement of OBCB (a) on the molecular plane ((*b,c*) plane) and (b) along the stacking axis ((*a,c*) plane). Molecules A and B denote the molecule as it is and its inverted form, respectively.

TABLE 1: Crystallographic Parameters of OBCB

formula	$C_{25}H_{12}OS_3$
crystal system	triclinic
space group	$P\bar{1}$
molecular symmetry	C_1
a (Å)	3.8200(5)
b (Å)	12.841(1)
c (Å)	18.385(2)
α (°)	95.915(9)
β (°)	92.545(10)
γ (°)	94.071(10)
V (Å³)	893.7
Z	2
density	1.577

3. Results and Discussion

3.1. Crystal Structure. Table 1 shows the crystallographic parameters of OBCB.[4] OBCB crystallizes in the space group $P\bar{1}$ with a molecular symmetry of C_1. The ORTEP plot is shown in Figure 2 together with the direction of the dipole moment (μ_D). The molecule is entirely planar and characterized by a dipole moment of about 1.56 D due to C_1 symmetry. Figure 3, parts a and b show the molecular arrangement on the molecular plane ((*b,c*) plane) and along the stacking axis ((*a,c*) plane),
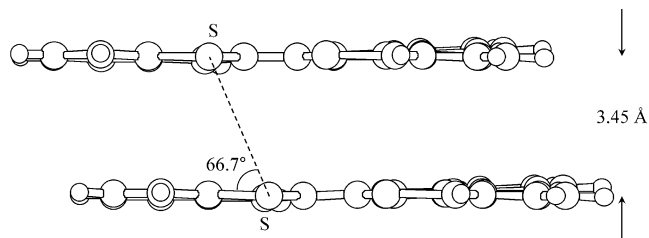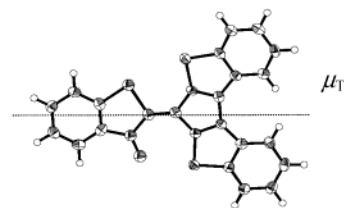

Figure 4. Overlap of two molecules along the stacking *b*-axis.

TABLE 2: Calculated and Observed Absorption Bands of OBCB

	calculated		observed	
	λ (nm)	f	λ (nm)	$\log \epsilon$
1st $\pi-\pi$*	393.3	0.790	508.6	4.31
2nd $\pi-\pi$*	294.2	0.450	388.6	4.12

μ_T: Transition dipole for 1st and 2nd transitions

respectively. The polar molecules are arranged in such a way as to cancel the dipole moment so as to electrostatically stabilize themselves. The molecules of the one form denoted by A are stacked in one column, while the inverted molecules designated by B are likewise arranged in the neighboring column.

The overlap of two molecules along the stacking *b*-axis is shown in Figure 4. The molecules are stacked with an interplanar distance of 3.45 Å, and the slip angle between two molecules amounts to 66.7°.

3.2. MO Calculations. Table 2 shows the calculated and observed absorption bands in solution together with the direction of the transition dipole (μ_T). The first $\pi-\pi$* electronic transition in the longest wavelength-region is expected to appear around 393.3 nm with an oscillator strength of about 0.79. The direction of the present transition dipole points along the long-molecular axis as shown in the form of a dotted line in the inset. The second strongest $\pi-\pi$* transition is supposed to appear around 294.2 nm with an oscillator strength of about 0.45. The direction of the transition dipole is again nearly along the long-molecular axis.

3.3. Solution Spectrum and Diffuse Reflectance Spectrum on Powders. Figure 5, parts a and b show the solution spectrum in acetonitrile and diffuse reflectance spectrum of OBCB, respectively. There are two broad absorption bands peaking at 510 and 380 nm in solution. These bands are assigned to the first and second $\pi-\pi$* electronic transitions as predicted by MO calculations (Table 2). The calculated absorption bands are appreciably overestimated toward shorter wavelengths. This is typical of ZINDO calculations and is attributed to the parameters selected from small molecules. Nevertheless, the direction of the transition dipole is quite reliable according to our experience of polarized reflection measurements on single crystals of various organic compounds. It is also remarkable to note that the molar extinction coefficient of OBCB is as high as ca. 20 000.

The absorption bands in powders before grinding are slightly displaced toward longer wavelengths. However, one-to-one correspondence of the absorption bands is possible, indicating
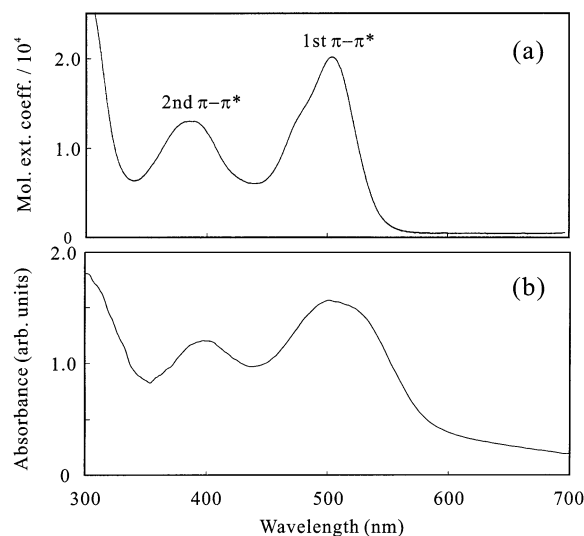
Piezochromic Indigoid

J. Phys. Chem. B, Vol. 107, No. 46, 2003 **12637**

Figure 5. (a) Solution spectrum of OBCB in acetonitrile and (b) diffuse reflectance spectrum measured on powdered OBCB.

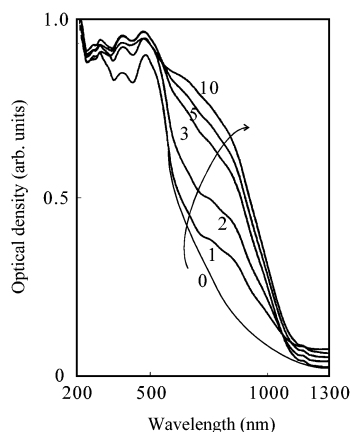**Figure 6.** Diffuse reflectance spectra of OBCB as a function of grinding time.

Figure 7. Powder X-ray diffraction diagrams before and after grinding.
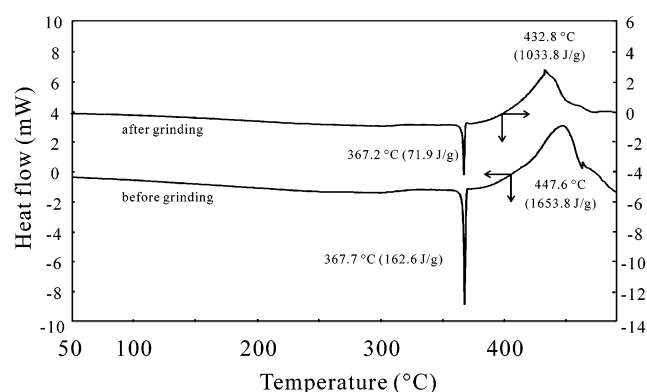
Figure 8. DSC measurements for powdered OBCB before and after grinding.

that the molecular nature is well preserved even in the solid state of powders.

On the other hand, grinding in a mortar with a pestle brings about significant spectral changes in the wavelength region between 600 and 1200 nm as shown in Figure 6. A new absorption band begins to appear around 750 nm and grows up with increasing grinding-time; whereas the absorption bands below 600 nm remain relatively unchanged. The present band around 750 nm is obviously caused by intermolecular inter-actions, because this band cannot be assigned to any molecular bands shown in Figure 5(a). It is also to be noted that the above band disappears when heated at about 280 °C for about 2 h or immersed in organic solvents such as methanol for several minutes. The present color change between red and black occurs reversibly.

3.4. Change in Molecular Arrangement. Figure 7, parts a and b show the powder X-ray diffraction diagrams before grinding (red phase) and after grinding (black phase), respectively. The diffraction peaks before grinding can mostly be assigned to those of the structure determined on single crystals.[4] On the other hand, the lattice is significantly disturbed by mechanical grinding (or shearing stress) as shown by reduced intensity in diffraction peaks. However, two new diffraction peaks appear around $2\theta = 23.4$ and $26.6°$. In particular, the diffraction peak around $2\theta = 26.6°$ (interplanar distance = 3.35
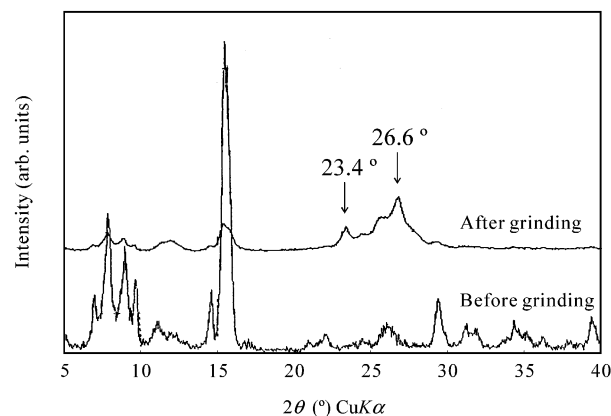
Å) indicates a new molecular ordering along the stacking axis. This suggests that the molecules are presumably slipped due to mechanical shearing and thus rearranged with a shorter inter-planar distance along the molecular stack ($2\theta = 26°$ (3.43 Å) → 27° (3.35 Å)). Because most of the diffraction peaks in the red phase can still be retained in the black phase, the black phase is characterized by a mixed state composed of the original red phase and a state in which the molecules are partly rearranged as a result of mechanical shearing.

3.5. DSC Measurements. Figure 8 shows the heat flow of the OBCB samples before and after grinding plotted as a function of temperature. The endothermic peak of the black phase occurs at a slightly lower temperature (367.2 °C) than the red phase (367.7 °C). The total endothermic energies are 71.9 and 162.6 J/g, respectively. The exothermic peak in the black phase also appears at a lower temperature (432.8 °C; 1033.8 J/g) than it does in the red phase (447.6 °C; 1653.8 J/g). The present results evidently indicate that the cohesion force (i.e., lattice energy) in the black phase is smaller than in the red phase, and the former is accordingly more stable than the latter. Therefore, the black phase can be regarded as a meta-stable state. On the other hand, the red phase is characterized by a thermodynamically stable state.

3.6. Polarized Reflection Spectra Measured on Single Crystals. Figure 9 shows the polarized reflection spectra of OBCB measured on the (001) plane of OBCB single crystals together with its projection onto the (*a,b*) plane. Polarized light was introduced with an angle of 18° with respect to the *a* axis for polarization parallel (nearly *a*) or perpendicular (nearly ⊥*a*) to the calculated transition dipole as shown in the inset of Table 2.
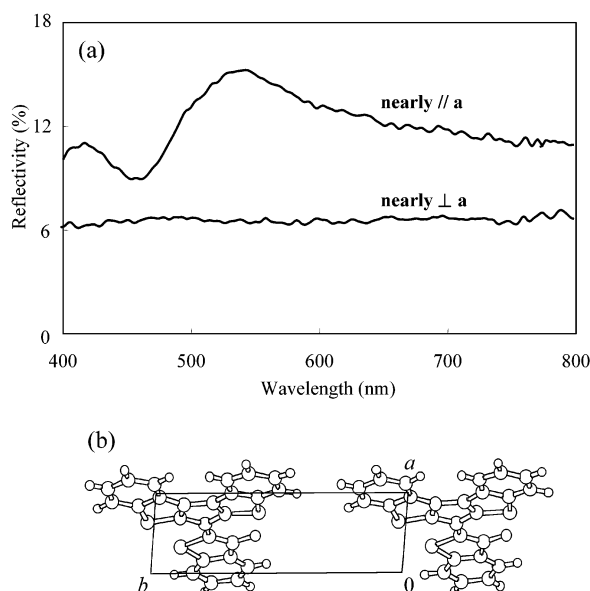
Figure 9. (a) Polarized reflection spectra measured on the (001) plane of OBCB single crystals and (b) projection of the crystal structure onto the (*a,b*) plane.

A prominent reflection band appears around 540 nm together with a small band around 420 nm for polarization parallel to the nearly *a*-axis. This is the direction along the first and second $\pi-\pi^*$ electronic transitions as described in Section 3.2 (see also inset in Table 2). On the other hand, these intense bands are completely quenched for polarization perpendicular to the nearly *a*-axis. The above results clearly indicate that the direction of both transition dipoles points along the long-molecular axis and is in good agreement with the result of MO calculations. Furthermore, the present polarized reflection spectra coincide with the diffuse reflectance spectrum measured on powders (Figure 5b).

3.7. Assignment of the Band Around 750 nm Due to Mechanical Grinding. When an excitation induces a transition dipole in the molecule, the excited state in crystals involves wave functions with significant probabilities on nearest neighbors. Therefore, the exciton coupling may well involve energy contributions from interactions with all of these nearest neighbor molecules acting in concert in the lattice. This may lead to the band splitting of the excited state or spectral displacement toward longer wavelengths or shorter wavelengths. The interaction energy ($\Delta E_{\text{exciton}}$) is given by the dipole−dipole equation[7,8] $\Delta E_{\text{exciton}} = |\mu_T|^2 (1-3\cos^2 \theta)/r^3$, where the transition dipole is denoted by μ_T and the distance and angle between two transition dipoles by r and θ, respectively. As evident from the present equation, the overall spread or shift energy is determined by the strength of the interneighbor coupling ($|\mu_T|^2$) which directly depends on the absorption coefficient of the molecule as well as the mutual relative orientation of the transition dipoles in molecular assemblies. That is, the term ($1-3\cos^2 \theta$) determines the geometrical relationship of transition dipoles correlated with the crystal structure. The bathochromic or hypsochromic shift depends on the critical angle of $\theta = 54.7°$, below which the former will result ("head-to-tail-like" arrangement) and above which the latter will be the case ("parallel-like" arrangement). The present excitonic interaction is especially significant in colorant or pigment systems,[9−11] because the absorption coefficient of the component molecule (i.e., square of the transition dipole) is quite high.

The band around 750 nm appears as a result of mechanical grinding and is obviously due to intermolecular interactions,

because no assignment is possible on the basis of the molecular absorption bands in solution, as stated in Section 3.3 (Figure 5a). Because the absorption coefficient of OBCB molecule is quite high over 20 000 as seen from Figure 5a, it is highly probable that the interactions between transition dipoles causes a new absorption band to appear around 750 nm. The present interpretation is also borne out by the results of X-ray diffraction diagrams. As discussed in section 3.4, the black phase is characterized by a mixed state of the initial red state and a new system in which the molecules are slipped due to mechanical shearing, resulting in a shorter interplanar distance (3.43 → 3.35 Å). This suggests that the molecules are arranged with a smaller slipping angle (i.e., more head-to-tail-like arrangement), leading to a the appearance of a new absorption band around 750 nm. Then, the new band covers the whole visible region together with the bands of the red phase. This makes the color black.

3.8. Mechanism of the Piezochromic Effect. Becausee the OBCB molecule is quite rigid and the molecular absorption bands are well preserved in the solid state in the visible region between 350 and 600 nm even after mechanical grinding (Figures 5 and 6), the piezochromic effect is obviously not caused by changes in molecular conformation but is due to intermolecular interactions caused by molecular rearrangement. In fact, mechanical grinding brings about reorganization of the molecules along the stacking axis (Figure 7). Under the present reorganized molecular arrangement, a new band appears around 750 nm due to interactions between transition dipoles. The color recovers from black to red due to heat treatment at about 280 °C, or solvent treatment. This can be explained in such a way that the disturbed lattice can be relaxed due to the lattice vibration at about 280 °C, or the solvent may loosen the crystal lattice, thus allowing the molecules to slide and/or rotate to find an energetically more stable site in the initial state.

4. Conclusions

The mechanism of the piezochromic effect of OBCB has been investigated from the structural point of view. The conclusions can be summarized as follows:

The red phase before grinding process is a thermodynamically stable state and coincides with the crystal structure analyzed on single crystals. On the other hand, the black phase as prepared by mechanical shearing is a meta-stable state.

The red color of the initial phase becomes black due to the appearance of a new band around 750 nm. The present band is structure-sensitive and is interpreted as arising from interactions between transition dipoles arranged in a head-to-tail-like fashion. The recovery of the color from black to red is ascribed to the relaxation of the disturbed lattice due to heat treatment or solvent treatment.

References and Notes

(1) Tanaka, M.; Tanifuji, N.; Hatada, S.; Kobayayshi, K. *J. Org. Chem.* **2001**, *66*, 803.

(2) Tanaka. M.; Kobayashi, K. *Chem. Commun.* **1998**, 1965.

(3) Mizuguchi, J. *Krist. Tech.* **1981**, *16*, 695.

(4) Kobayashi, K.; Tanifuji, N.; Mizuguchi, J. *Z. Kristallogr. NCS* **2002**, *217*, 521.

(5) WinMOPAC Ver.3, Fujitsu.

(6) M. C. Zerner, *ZINDO, A General Semiempirical Program Package.* Department of Chemistry, University of Florida, Gainesville, FL.

(7) Kasha, M. *Spectroscopy of the Excited State*; Plenum Press: New York, 1976; p 337.

(8) Craig, D. P.; Walmsley, S. H. *Excitons in Molecular Crystals*; W. A. Benjamin, Inc.: Reading, MD, 1968.

(9) Endo, A.; Matsumoto, S.; Mizuguchi, J. *J. Phys. Chem. A* **1999**, *103*, 8193.

(10) Mizuguchi, J. *J. Phys. Chem. A* **2001**, *105*, 1121.

(11) Mizuguchi, J.; Tojo, K. *J. Phys. Chem. B* **2002**, *106*, 767.