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Structure and Absorption Spectra of Thin Films of Tripmenodithiazine, $C_{18}N_2S_2H_{10}$

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STRUCTURE AND ABSORPTION SPECTRA OF THIN FILMS OF TRIPHENODITHIAZINE, $C_{18}N_2S_2H_{10}$

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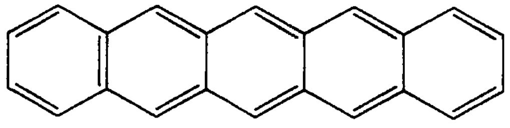
Abstract A crystal structure of triphenodithiazine (TPDT) has been determined by the X-ray diffraction of a single crystal; Crystal data were monoclinic, space group P21/c, a= 10.4814(12) Å, b= 5.4203(7) Å, c= 12.3871(17) Å, β = 107.554 (10)°, V= 670.969 Å^3 and Z= 2. The X-ray diffractions of the powder and the thin film of the compound have also been studied at room temperature. Sharp diffraction lines of the thin film with thickness of 500 Å, 100, 200, 500 and 600 lines were found. The TPDT molecules in this film arrange along the a*-axis perpendicular to the substrate. The absorption spectra of several thin films with thickness of 150 Å, 500 Å, 700 Å, 900 Å and 1200 Å have been studied at room temperature. The spectra of thin films were very sensitive to the molecular arrangement. A new sharp absorption band at around 686 nm was observed for the oriented films of the 500 Å, 700 Å and 900 Å. This behavior observed in the oriented film may arise from the Davydov splitting. When the oriented film of TPDT was exposed to bromine gas, the color of the film changed remarkably. Then the new absorption band was observed at around 800 nm. The thin film exposed to bromine gas showed a broad diffraction peak at around 2θ= 27°. This thin film became mostly amorphous.

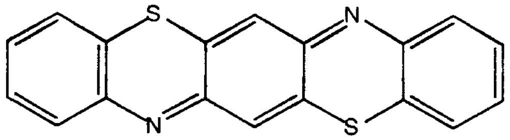
Key Word: Evaporated thin film, structure, absorption spectra, triphenodithiazine, electronic state

INTRODUCTION

Maruyama has studied electrical and optical properties of oriented and amorphous thin films of many aromatic hydrocarbons.[1-3] I (I.Shirotani) have investigated the electronic spectra of thin films of several aromatic compounds as a co-worker of prof. Maruyama.[4-6] A remarkable feature of the electronic spectra of aromatic crystals is the



Pentacene



Triphenodithiazine (TPDT)

FIGURE 1 Molecular structures of pentacene and triphenodithiazine(TPDT).

appearance of the Davydov splitting.[7] As the Davydov splitting of tetracene and pentacene is very large, we can see the Davydov splitting in the oriented thin films of these compounds. The Davydov splitting of the 0-0 band in the oriented films is 620 cm^{-1} for tetracene[8] and 950 cm^{-1} for pentacene.[5,9] This splitting disappears in the amorphous films of both compounds.[9]

Figure 1 shows molecular structures of pentacene and triphenodithiazine ($C_{18}N_2S_2H_{10}$; TPDT). The structure of a TPDT molecule is similar to that of pentacene which shows the anomalous optical[9] and electrical behavior[10,11] at high pressures. The TPDT is an interesting heterocyclic aromatic compound containing nitrogen and sulfur atoms. The resistivity of the compound rapidly decreases with increasing pressure, lowering to ca. 5×10^2 Ωcm at around 22 GPa.[12] The thin films of TPDT are easily prepared by evaporation onto a glass or quartz substrate in a vacuum.

An ionization potential of the thin film of TPDT is 5.12 eV[12], which is comparable to that of TTF(5.0 eV).[13] Thus, TPDT molecules in the film act on as a good electron donor, and form the charge transfer complexes with various electron acceptors. The thin film of TPDT sensitively reacts to the acidic gases such as bromine. Then, a color of TPDT sharply changes purple to blue when the film is exposed to the bromine gas.

In this paper we present some results of the X-ray diffraction of the single crystal, powder and thin films of TPDT, and the absorption spectra of thin films of the compound, and discuss the relation between the structure and the absorption spectra of the thin films.

EXPERIMENTAL

The compound TPDT has already been synthesized by Nishi et al.[14,15] The compound was purified by repeated recrystallization from xylene or dimethylformamide. The thin films of TPDT were prepared by evaporation onto a quartz or a glass substrate held at room temperature in a vacuum of 1.33×10^{-4} Pa(10^{-6} Torr). The thickness of the film was monitored by means of a quartz-crystal oscillator. The absorption spectra of the evaporated films were measured with a Hitachi 330 spectrophotometer. The X-ray diffractions of the powder and the thin film of TPDT were studied at room temperature using a Rigaku RU-200B diffractometer with a Cu-K_α radiation source.

The plate-shaped golden metallic crystals were slowly grown in a xylene solution. Intensity data of the crystal with dimensions of $0.04\times0.1\times0.23$ mm were measured on a Rigaku four-circle diffractometer using graphite-monochromatized Mo-K_α radiation source. Reflections with θ max= 30° were collected in the ω-2θ scan mode. Three standard reflections measured every 50 reflections showed no decrease in the intensity. The reflections were corrected for Lorentz and polarization effects but not for absorption effect. The structure has been easily solved by Patterson method since a molecule sits on a inversion symmetry center at the origin. The refinements of atomic parameters were carried out by a block-diagonal least-squares method on the basis of F magnitude with a unit weight for all reflections. Anisotropic thermal parameters for non-hydrogen atoms were used. Atomic scattering factors for the non-hydrogen atoms were taken from International Table for X-ray Crystallography[16] and those for hydrogen atoms from the data reported by Stewart et al.[17] The R factor converged to 0.041 for 1274 independent reflections with $F>3\sigma(F)$. The atomic coordinates are given in Table 1.

Crystal Data: $C_{18}N_2S_2H_{10}$, M= 318.41, monoclinic, space group P21/c,
a= 10.4814(12) Å, b= 5.4203(7) Å, c= 12.3871(17) Å, β= 107.554(10)°,
V= 670.969 Å^3 and Z= 2.

RESULTS AND DISCUSSION

[Crystal Structure]

The crystal structure of TPDT is shown in Fig.2. The bond distances and bond angles for a TPDT molecule, and selected intermolecular distances between TPDT

TABLE 1 Fractional atomic coordinates for the TPDT molecule

Atom	*X*	*Y*	*Z*
S	0.20919(7)	0.31412(13)	-0.07903(6)
N	0.1233(2)	0.3738(2)	0.1435(2)
C(1)	0.0281(2)	-0.0443(5)	-0.1015(2)
C(2)	0.0943(2)	0.1413(4)	-0.0347(2)
C(3)	0.0685(2)	0.1984(5)	0.0726(2)
C(4)	0.2211(2)	0.5284(5)	0.1263(2)
C(5)	0.2709(2)	0.5194(5)	0.0328(2)
C(6)	0.3708(3)	0.6817(6)	0.0262(2)
C(7)	0.4206(3)	0.8549(5)	0.1100(2)
C(8)	0.3708(3)	0.8711(5)	0.2006(2)
C(9)	0.2728(3)	0.7083(6)	0.2082(2)
H(1)	0.054(3)	-0.079(6)	-0.175(2)
H(6)	0.401(3)	0.664(5)	-0.040(2)
H(7)	0.488(3)	0.962(5)	0.109(2)
H(8)	0.409(3)	0.995(6)	0.263(2)
H(9)	0.234(3)	0.719(6)	0.260(2)

molecules are given in Table 2. TPDT molecules on the inversion symmetry center at the origin are stacked face to face along the b-axis with equivalent interplanar distance of 3.47 Å. Figure 3 shows the overlapping mode between the neighbor molecules of TPDT. The tilting about 45° of the long molecular axis against the b-axis leads to the overlapping between adjacent molecules with the displacement of about one and half benzene rings along the long molecular axis.

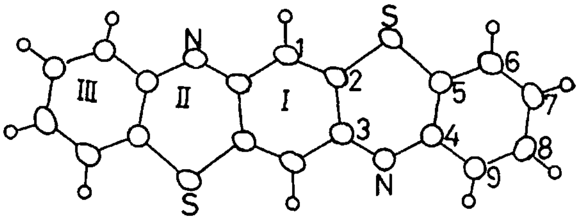
Short intermolecular contacts within a column are observed between S...N^{iii} and N...C(2^{iii}) with atomic distances of 3.737(2) and 3.475(3) Å, respectively. Molecules between adjacent columns along the c-axis cross each other and C(1)-H(1) coordinates to the lone pair of N atom of a molecule in the adjacent column. The C(8)-H(8) bond in the end of a TPDT molecule is directed toward π-electron cloud above C(7) of benzene ring of an adjacent molecule with H(8)...C(7^{v}) atomic distance of 2.79(3) Å to form CH/π interaction between them.[18)] The dihedral angles between planes I...II and planes II...III of 1.26° and 1.86°, respectively indicate that a molecule has a little twist. In the ring II containing S and N atoms, a bond angle of C (2)-S-C(5) is 102.7°. Bond distances of S-C(2) and S-C(5) are equivalent while bond distances of C(3)-N and C(1)-C(2) are shorter than those of counterpart C(4)-N and C(3)-C(1^{i}), respectively. The formers C(3)-N and C(1)-C(2) have higher percentage of double bond character, and unsymmetrical electron distribution is also observed in a pentacene.[19)]

[Structure of Thin Film]

Figure 4 shows the powder X-ray diffraction profile of the TPDT. The diffraction

TABLE 2 Bond distances (Å) and selected bond angles (°) for the TPDT molecule and selected intermolecular contacts (Å) with e.s.d.'s in parentheses.

Bond distances



S-C(2)	1.740(3) Å	C(1)-C(2)	1.353(3) Å	C(5)-C(6)	1.388(4) Å
S-C(5)	1.741(2)	C(2)-C(3)	1.468(4)	C(6)-C(7)	1.380(4)
N-C(3)	1.304(3)	C(3)-C(1^{i})	1.438(4)	C(7)-C(8)	1.375(5)
N-C(4)	1.389(4)	C(4)-C(5)	1.408(4)	C(8)-C(9)	1.378(4)
				C(4)-C(9)	1.394(4)

Selected bond angles

C(2)-S-C(5)	102.7(1)°	dihedral angles	
S-C(2)-C(3)	120.4(2)	plane I · · · plane II	1.26°
C(2)-C(3)-N	126.8(2)	plane II · · · plane III	1.86°
C(3)-N-C(4)	122.2(2)	plane I · · · plane III	2.73°
N-C(4)-C(5)	125.4(2)		
C(4)-C(5)-S	122.4(2)		

Intermolecular short contacts within a column

S ...N^{iii}	3.737(2) Å	C(8) ...C(3^{ii})	3.560(4) Å
N ...C(2^{iii})	3.475(3)	C(9) ...C(1^{iii})	3.535(4)
C(5) ...C(1^{ii})	3.505(3)	C(9) ...C(3^{ii})	3.506(4)

Between columns

S ...N^{iv}	3.434(2) Å	N^{i}H(1) ...N^{iv}	2.80(3) Å
H(8)...C(7^{v})	2.79(3)		

symmetry code: none x, y, z; (i) -x, -y, -z; (ii) x, l+y, z;
(iii) -x, l-y,-z; (iv) x, 0.5-y, -0.5+z;
(v) l- x, 0.5+y, 0.5-z:

lines were indexed from the results of the X-ray diffraction of the single crystal. The lattice parameters obtained from these data were a= 10.49(7) Å, b= 5.428(7) Å, c= 12.39(6) Å, β= 107.7(7)°, V= 672.0(5.1) Å^3.

Figure 5 shows the X-ray diffraction profile of a thin film of TPDT, the thickness of which is about 500 Å. Sharp diffraction lines were observed for the 500 Å film. The profile comprises harmonic lines assigned to the n00 (n= 1, 2, 5 and 6) reflections, with

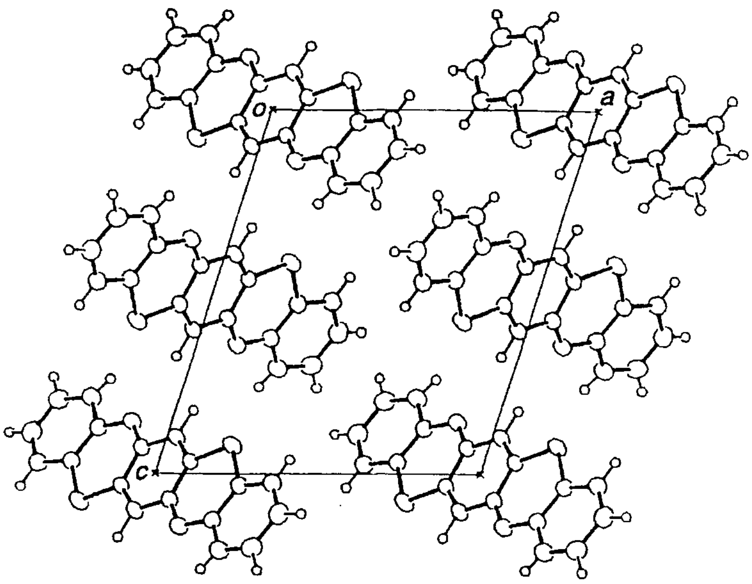


FIGURE 2 Projection of the structure along the b-axis.

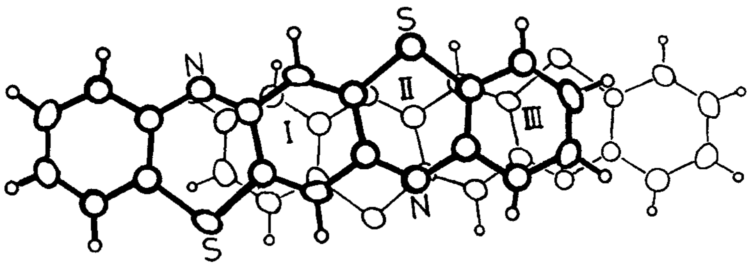


FIGURE 3 Overlapping mode between molecules with numbering of atoms.

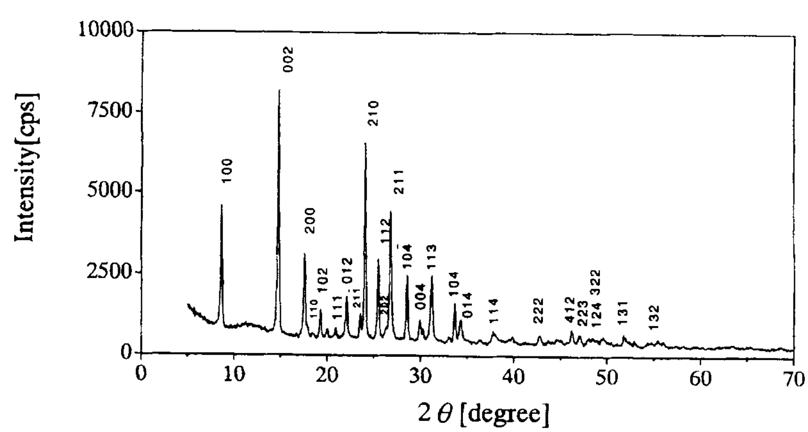


FIGURE 4 Powder X-ray diffraction pattern of TPDT at room temperature.

no other reflections. As is shown in Fig.5, the 300, 400, 500 and 600 lines were not found in the powder X-ray diffraction pattern of TPDT. Especially, the intensity of 300 and 400 lines measured by the X-ray diffraction of the single crystal was very weak. The both lines in the 500 Å film were buried in the broad amorphous pattern of the glass substrate observed at around $2\theta = 27°$. Thus, TPDT molecules orient in the film, and arrange along the a*-axis perpendicular to the substrate. The similar results were also obtained for the 700 Å and 900 Å films. Figure 6 shows the X-ray diffraction pattern of the thin film of 1200 Å. This film had the strong broad diffraction peak at around $2\theta = 27.5°$ in addition to the sharp lines of 100 and 200. The strong broad peak is mainly due to the disorder of the arrangement of TPDT molecules in this film. The width of 100 and 200 lines of the 1200 Å film is broader than that of the 500 Å film. The 500 and 600 lines observed in the 500 Å film were missing for the 1200 Å film. Thus, there are the amorphous and oriented states in this film. When a rate of evaporation of the compound is quick, an amorphous film of TPDT can easily be prepared.[12)]

[Absorption Spectra of Thin Film]

Figure 7 shows the absorption spectra of three thin films of TPDT with thickness of 150, 500 and 1200 Å. The absorption spectra of these films are sensitive to thickness of the film. The 150 Å film showed the broad spectrum in the 450-650 nm region. This spectrum roughly corresponds to that of a chlorobenzene solution of TPDT.[12)] The new absorption peak at around 686 nm appeared in the spectra of the 500, 700 and 900 Å films. The TPDT molecules in these films show the oriented arrangement on the substrate. On the other hand, the absorption spectrum of the 1200 Å film shows that the absorption intensity at around 470 nm increased remarkably, and the intensity of the new band decreased compared with that of the oriented films. As mentioned above, the molecular arrangement in the 1200 Å film is partially amorphous. The new peak at around 686 nm disappear in the amorphous film. The absorption spectra of the thin films strongly depend on the crystallinity in the thin film.

The electronic spectra of molecular crystals differ from those of corresponding free molecules. One of the prominent features of the spectra of the crystals is the shift of the absorption band toward longer wavelength, and the other is the appearance of the Davydov splitting. The absorption spectra of single crystals of tetracene have already been studied.[7)] The Davydov splitting of the 0-0 band of the compound is about 575 cm^{-1} for the single crystal. This large splitting is fortunately discernible even for the oriented film with the use of unpolarized light. The Davydov splitting of the 0-0 band of

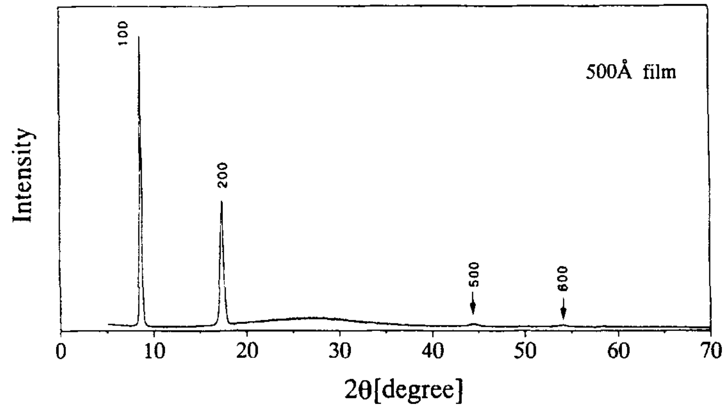


FIGURE 5 X-ray diffraction profile of the thin film of TPDT with thickness of 500 Å.

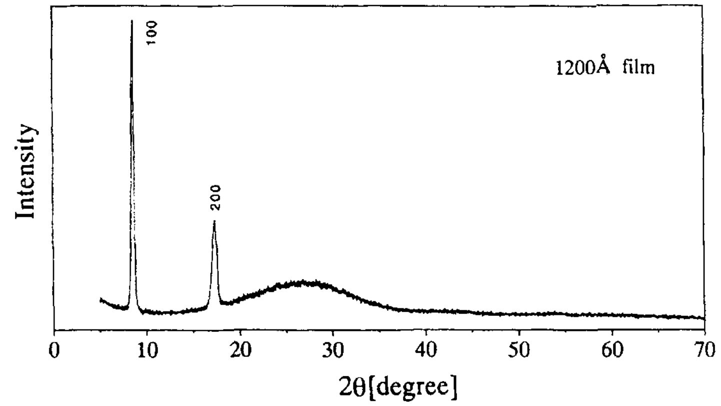


FIGURE 6 X-ray diffraction profile of the thin film of TPDT with thickness of 1200 Å.

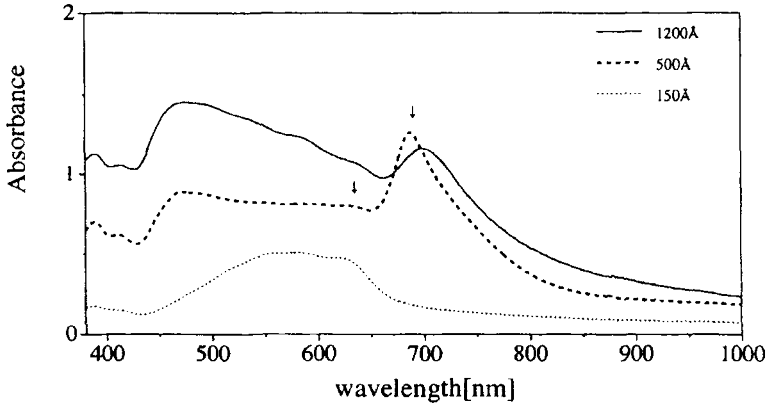


FIGURE 7 Absorption spectra of several thin films of TPDT with thickness of 150 Å, 500 Å and 1200 Å at room temperature.

pentacene is about 950 cm^{-1} for the oriented film. The Davydov splitting in the both oriented films increases with increasing pressure at the rate of 370 cm^{-1}/GPa for tetracene and 700 cm^{-1}/GPa for pentacene.⁹⁾ The Davydov splitting of both compounds disappears for the amorphous film. Two absorption bands in a thin film of tetraselenotetracene($C_{18}H_8Se_4$) are observed at around 650 nm and 840 nm.²⁰⁾ Both bands of the film do not correspond to the band in the solution spectrum. The peak at 640 nm in the film was insensitive to pressure; on the contrary the 840 nm band shows a large red-shift at the rate of 1200 cm^{-1}/GPa. The large Davydov splitting has been found for the thin film of the compound containing selenium.²⁰⁾

The space group of TPDT crystal is P21/c, Z= 2. TPDT molecules are stacked face to face along the b-axis. Since the distance between TPDT molecules within a column is significantly short (3.47 Å), the intermolecular interaction is considerably strong. Thus, the large Davydov splitting can be expected for the TPDT. As is shown in Fig.6, four sharp diffraction lines, 100, 200, 500 and 600 lines, were found for the 500 Å, 700 Å and 900 Å films. Thus, the molecular excitons can easily propagate in these oriented films. The new band at around 686 nm was very sensitive to the molecular arrangement in the film. As is indicated by the arrows in Fig.7 the absorption spectra of the oriented film may split in two bands. The magnitude of the splitting is about 1100 cm^{-1} for the 500 Å, 700 Å and 900 Å films. This value is comparable to the Davydov splitting of pentacene. The absorption spectrum of the amorphous film differs from that of the oriented film. The new peak at around 686 nm disappears in the amorphous film.¹²⁾ Thus, we suggest that two bands shown by the arrows may arise from the Davydov splitting of TPDT. The absorption spectrum of the 1200 Å film is due to the coexistence of the oriented and amorphous states.

Figure 8 shows the absorption spectra of the oriented films of TPDT exposed to bromine gas at room temperature. The new band which is not found for the original film appeared at around 800 nm. Then, the color of the oriented film sharply changed from gold(reflected light) to blue when the film was exposed to the gas. Similar results were also found even if the film of TPDT was exposed to HCl or NO_2 gases. These phenomenona suggest that the film of TPDT can be used as an indicator or a sensor in order to detect these gases.¹²⁾ As mentioned above, the TPDT is the good electron donor. Thus, the new charge transfer complex was formed on the surface of the TPDT film when it was exposed to Br_2 gas. The X-ray diffraction pattern of this film showed the broad peak at around $2\theta = 27°$. The sharp diffraction lines of the oriented film were

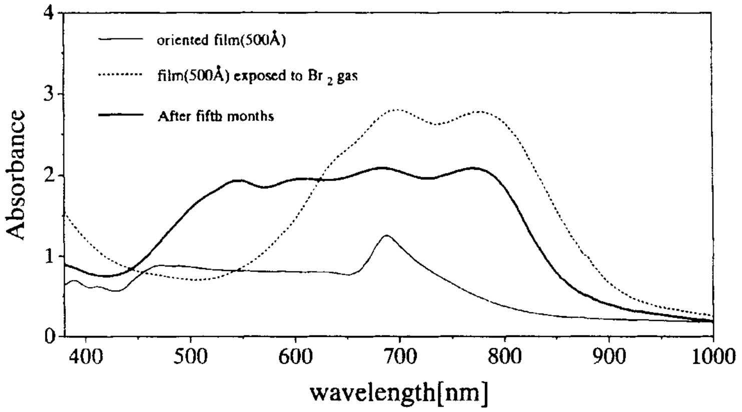


FIGURE 8 Absorption spectra of the oriented film(500 Å) and the oriented films exposed to bromine gas.

disappeared by the formation of the complex. The oriented film exposed to Br_2 gas became mostly amorphous. The absorption spectrum of the blue color film was measured again after fifth months. This spectrum is shown in Fig. 8. The absorption spectra of the film has slowly changed with time. The bromine was gradually released from the film at room temperature. When the blue color film was warmed to above 60 °C, the bromine was easily released from the film. Then, the new band disappeared, and the absorption spectrum of TPDT was observed only in the visible region. This spectrum is very similar to that of the amorphous film of TPDT.

DEDICATION

It is our pleasure to dedicate this paper to professor Yusei Maruyama who made a huge contribution to the field of physicochemical properties of organic evaporated films.

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