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Solid-state spectra of 5,7,12,14-tetrathiapentacene-6,13-dione

Shinya Matsumoto*, Hisashi Miura, Jin Mizuguchi

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

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Abstract

Solid-state absorption spectra of the title compound have been investigated in an effort to define the contribution of intermolecular interactions to the bathochromic shift associated with crystallization. In this regard, the bathochromic shift observed upon changing from the solution to the solid state was found to be relatively small in comparison to that observed with a closely related analogue. Studies involving the temperature dependence of the absorption spectra of evaporated thin films revealed that intermolecular interactions in the crystalline state had very little affect on the excited state properties of this dye. This probably accounts for the small bathochromic shift upon crystallization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Solid state spectrum; Tetrathiobenzoquinone; Intermolecular interactions; Bathochromic shift; X-ray diffraction; Temperature dependence

1. Introduction

Tetrathiobenzoquinone dyes **1**–**3** (Fig. 1) have a *para*-benzoquinone group as their chromophore and sulfur atoms and carbonyl moieties as the donor and acceptor groups, respectively. These dyes possess a typical cross-conjugated system and they have attracted attention as organic pigments because of their low solubility in various organic solvents and their interesting colors in the solid state [1]. Their ability to produce bathochromic shifts on switching from solution to the solid state greatly depends on the nature of the groups attached to the benzoquinone moiety. The bathochromic shift observed when the absorption spectrum of **2** was measured in solution versus the solid state was about 168 nm (6621 cm^{-1}), whereas the corresponding shift observed with **3** was about 47 nm (2101 cm^{-1}), despite of the minor differences in the molecular structures of **2** vs. **3**.

When the mechanism associated with the extremely large bathochromic shift observed upon crystallization of **2** was investigated with the aid of X-ray analysis, it was found that the spectral shift was caused by close intermolecular atomic contacts in the crystal structure [2]. In the case of **3**, intermolecular interactions in the solid state were found to be minimal, mainly because the additional –CH$_2$– group in the side chain

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* Corresponding author at present address: Supramolecular Science Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1, Hirosawa, Wako, Saitama 351-0198, Japan. Tel.: +81-48-467-9146; fax: +81-48-467-9389.
E-mail address: s-matsu@postman.riken.go.jp (S. Matsumoto).

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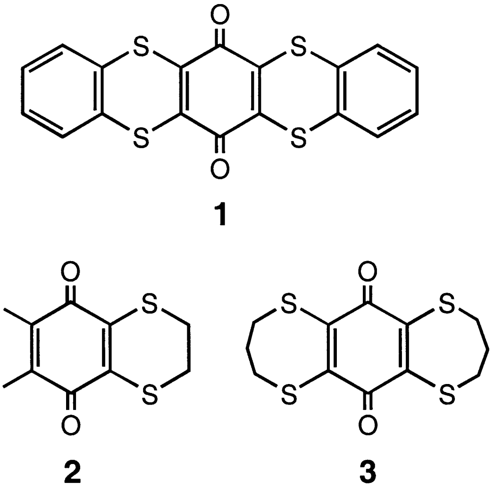

Fig. 1. Structures of dyes **1**–**3**.

altered the molecular shape of the dye and its intermolecular distances.

The incorporation of phenylene groups into the structure of **2** gives a dye (**1**) with an expanded conjugated system. In solution, the color of dye **1** is red, which is significantly different from the pale yellowish-green color of **2** and **3** in solution. On the other hand, the bathochromic shift upon changing from the solution to the solid state was relatively small [77 nm (2525 cm^{-1})].

In the present investigation, the solid state absorption spectra of **1** have been studied in order to elucidate the influence of intermolecular interactions on the shift in the position of absorption band. The experimental measurements were augmented by molecular orbital calculations.

2. Experimental

2.1. Sample preparation

Dye **1** was prepared by a published procedure [1]. Single crystals of this dye were obtained by recrystallization from benzene as dark-green very thin needles. Evaporated thin films were prepared using vacuum evaporation equipment (Tokyo Vacuum Co. Ltd., model EG240). Film samples used to record absorption spectra and X-ray diffraction patterns were evaporated onto glass slides and had thicknesses of 1000 and 3000 Å, respectively.

2.2. Measurements

UV/visible spectra were recorded on a Shimadzu UV-2400PC spectrophotometer. Diffuse reflectance spectra were recorded on a Varian CARY 5E spectrophotometer equipped with an integrating-sphere accessory. Samples were diluted with $BaSO_4$ (1% w/w). Reflectivity was transformed into optical density by the Kubelka-Munk equation. X-ray diffraction was measured by a Rigaku RINT-2000 diffractometer using graphite-monochromatic CuK_α radiation ($\lambda = 1.5415$ Å, 15 kW/h). Temperature dependence of the absorption spectra of evaporate films was measured using cryostat equipment (Iwatani Industrial Gases Corp., cold head: D105 and compressor: CW301) between 300 and 20 K.

2.3. Calculations

Molecular geometries were optimized using the MINDO/3 [3] Hamiltonian in the MOPAC 94 software package [4]. Electronic spectra were calculated using the INDO/S Hamiltonian in the ZINDO [5] software package. In these experiments, 197 configurations were considered for the configuration interaction (CI). All calculations were performed on a Power Macintosh 8500/120 computer.

3. Results and discussion

3.1. Solution and the solid-state spectra

Fig. 2 shows the absorption spectra of **1** in toluene and in the solid-state and Table 1 provides a summary of the experimental spectroscopic data for **1** together with calculated values. Dye **1** gave a pale red color in toluene that changed to moss green in the evaporated films. The observed bathochromic shift corresponded to 77 nm, which is considerably smaller than that observed for dye **2** (168 nm) [2].

The electronic properties of the optimized molecular structure of **1** were determined and it

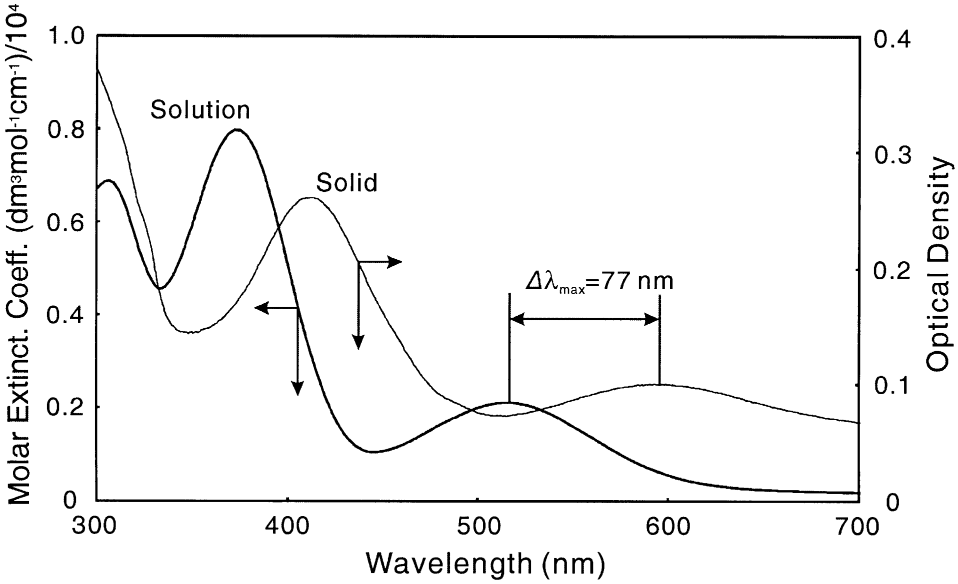

Fig. 2. Absorption spectra of **1** in toluene and in an evaporated thin film.

Table 1
Experimental and calculated absorption maxima for dye **1**

	Solution	Solid	Calculated
$\lambda_{\max}$ (nm)	515 (2100[a])	592	388 (0.1324[b]) $^1B_{2g}$[c] ($1a_{2u} \rightarrow 1b_{1g}$)
	372 (8000[a])	410	296 (0.1593[b]) $^1B_{1u}$[c] ($1a_{1u} \rightarrow 1b_{1g}$)

[a] Molar extinction coefficient (dm^3 mol^{-1} cm^{-1}).

[b] Oscillator strength.

[c] The excited state of the major composition of CI configurations.

was found that the dye belongs to the D_{2h} symmetry group. In addition, the HOMO to LUMO transition [$1b_{2u}(\pi) \rightarrow 1b_{1g}(\pi^*)$] was found to be symmetry forbidden. The longer wavelength band (515 nm) was assigned to the $\pi \rightarrow \pi^*$ transition involving the HOMO-2 (a_{2u}) to the LUMO (b_{1g}) as described in Table 1. The band near 372 nm was attributed to the $\pi \rightarrow \pi^*$ transition involving the HOMO-4 (a_{1u}) to the LUMO (b_{1g}). Both of these bands appeared at longer wavelengths compared to those observed for **2** and **3**, because of the expanded conjugated system. The direction of the dipole moment in the excited state of **1** was found to be along the short molecular axis (C=O direction) for the longer wavelength band and along the long molecular axis (perpendicular to the C=O direction and on the molecular plane) for the shorter wavelength band. Similar dipole moments were found for **2** and **3**.

3.2. X-ray diffraction and diffuse reflectance spectra

X-ray diffraction patterns for an evaporated thin film and single crystals of **1** are shown in Fig. 3a and b, respectively. Weak diffraction peaks were observed near 25° ($d \sim 3.5$ Å) in the evaporated thin film. These peaks correspond to the typical interplanar distances for aromatic compounds. The strong peak near 9° ($d \sim 10$ Å) probably results from the long-range ordering of dye molecules. The same peaks were observed in the diffraction pattern of single crystals (Fig. 3b).

Fig. 4 shows the diffuse reflectance spectrum obtained using single crystals of **1**. Two broad bands were observed near 415 and 600 nm, both of which were consistent with the results obtained using evaporated films. Examining data from diffuse reflectance spectra and X-ray diffraction experiments indicated that the phase of the evaporated dye film was the same phase as that in single crystals.

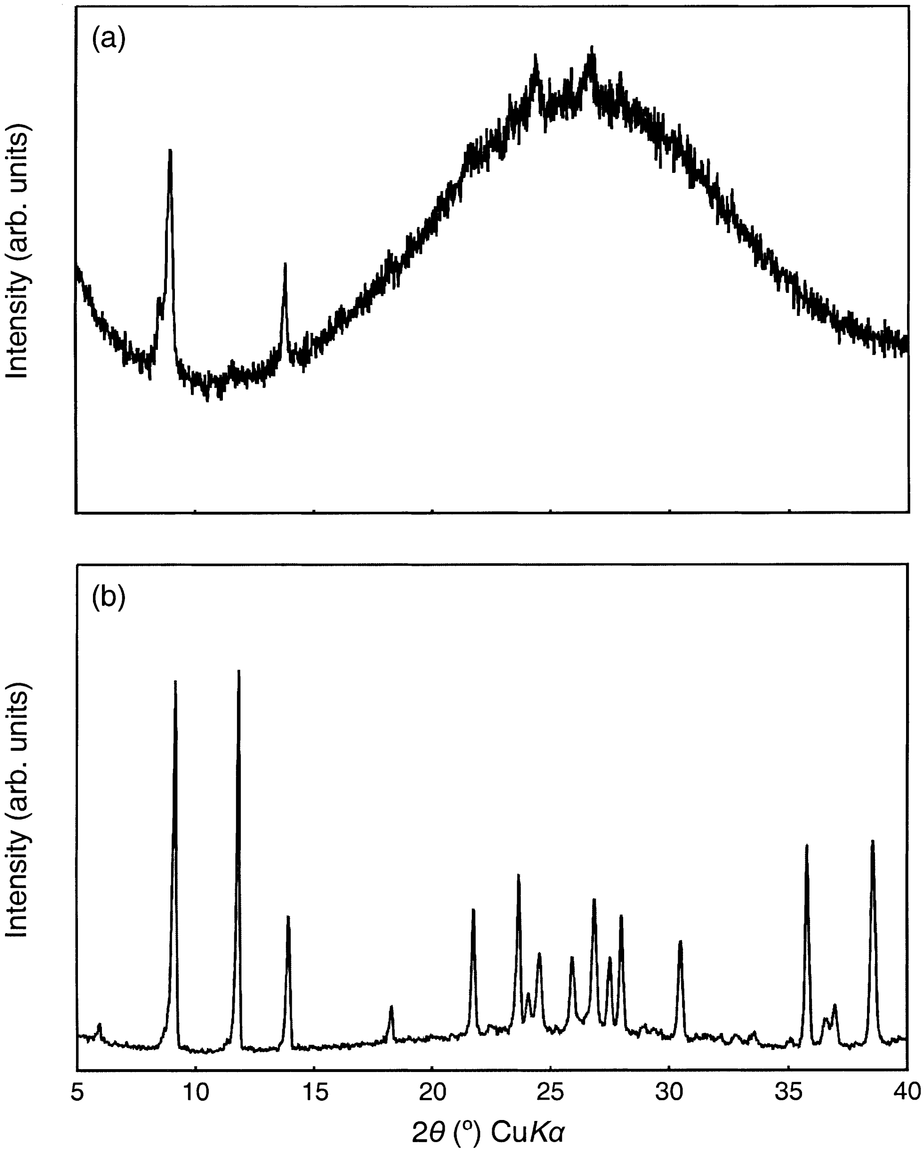

Fig. 3. X-ray diffraction patterns of (a) the evaporated thin film and (b) single crystals of dye **1**.

3.3. Temperature dependence of absorption spectra

At low temperature, the thermal motion of atoms decreases and causes a contraction of the crystal lattice. Consequently, intermolecular distances become shorter as the temperature is lowered. A well-known factor that influences the solid-state spectra of dyes and pigments is the interaction between transition dipoles, commonly referred to as exciton coupling effects [6,7]. Since the transition moment of frequently encountered dyes and pigments is usually large, this effect is often significantly influenced by the intermolecular distances and molecular arrangements [8,9]. The energy associated with these interactions is proportional to the inverse cube of the intermolecular distance.

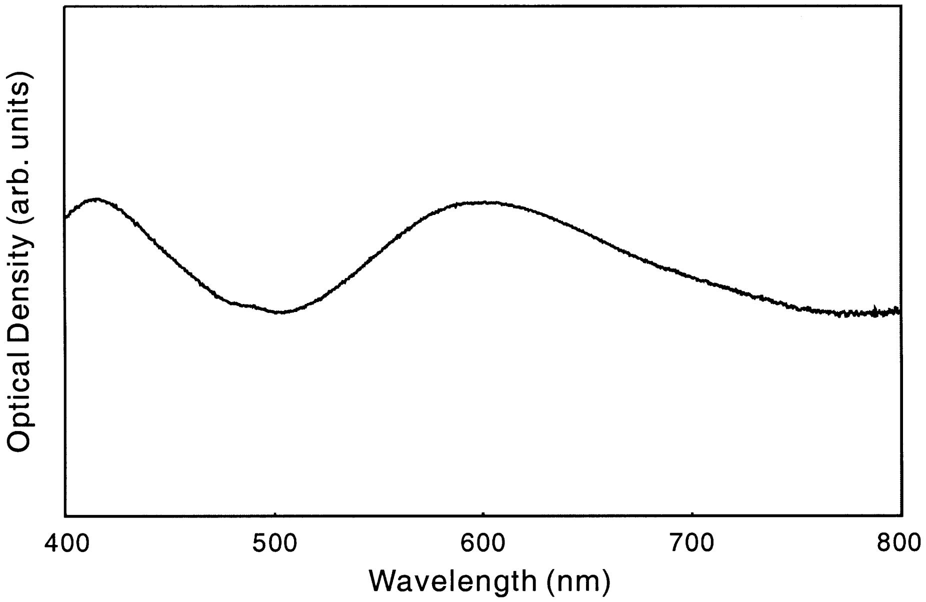

Fig. 4. Diffuse reflectance spectra of single crystals of **1**.

If the effect of these intermolecular interactions on the optical properties were large, temperature-dependent spectral shifts would be significant.

Fig. 5 shows the temperature dependence of the absorption spectra of an evaporated film of **1**. It is clear that the absorption bands were slightly displaced towards longer wavelengths as temperature decreased, suggesting that the contribution of intermolecular interactions in the excited state was not significant.

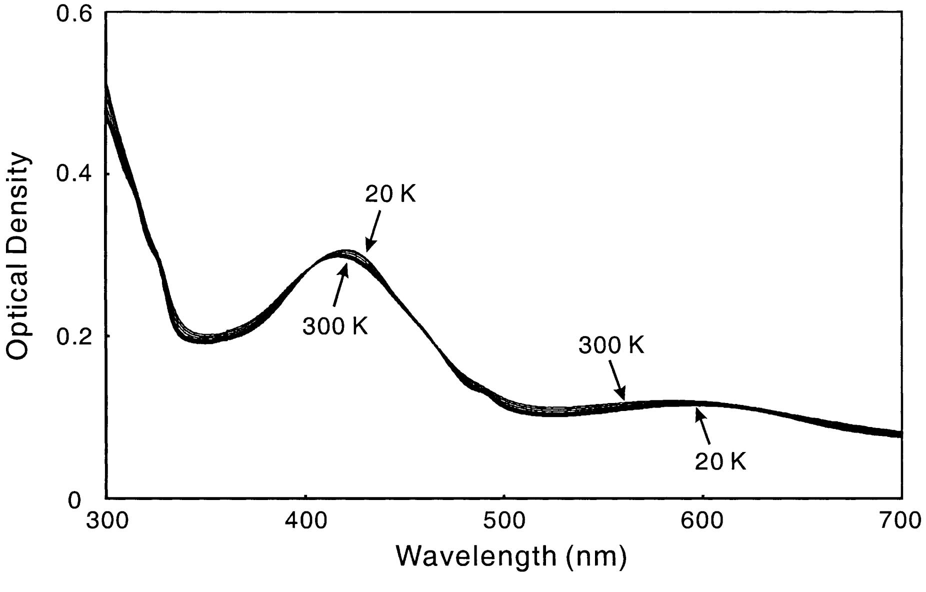

Fig. 5. Temperature dependence of the absorption spectra of **1** in an evaporated thin film.

3.4. Other effects

Close intermolecular atomic contacts between sulfur atoms are known to influence the electronic properties of dyes in the solid state [10–13], causing extremely large bathochromic shifts upon crystallization [2]. The effects of these contacts in dye **3** was found to be small because the intermolecular distance was enlarged due to the slightly larger side chain group in this dye versus **2** [2]. Accordingly, close intermolecular atomic contacts would not be expected in **1**, which has a significantly larger side chain than present in **3**. Therefore, we believe that the relatively small bathochromic shift upon crystallization of **1** can be attributed to weak intermolecular interactions in the excited state.

4. Conclusions

Results from a spectroscopic investigation involving the title compound indicate the following: (1) absorption bands in the visible region arise from the $\pi\rightarrow\pi^*$ transition, with the longer wavelength band corresponding to HOMO-2→LUMO transition; (2) evaporated films have the same phase as that of single crystals; and (3) the small bathochromic shift associated with the crystallization of the title compound is due to weak intermolecular interactions in the excited state.

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