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Interpretation of the Solid-State Spectra of Tetrathiabenzoquinone Derivatives from the Standpoint of Intermolecular Interactions

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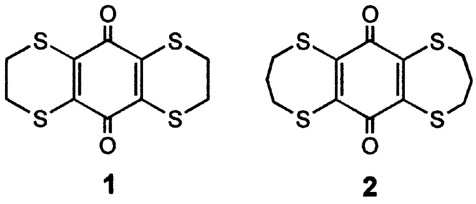
The solid-state spectra of two tetrathiabenzoquinone derivatives have been investigated from the standpoint of intermolecular interactions, while focusing on the bathochromic shift upon crystallization. These derivatives form a characteristic molecular arrangement consisting of a one-dimensional molecular column and a two-dimensional molecular sheet. Interactions in the excited state which depend on the molecular arrangement, exciton coupling effects (interactions between transition dipoles), were found to be small in both compounds. A small bathochromic shift of the trimethylenedithio derivative is attributed to these effects. The temperature dependence of the solid-state spectra is also in good agreement with the calculated result. However, an extremely large bathochromic shift of the ethylenedithio derivative cannot be explained in terms of the exciton coupling effects. Intermolecular interactions caused by the close atomic contacts between intermolecular sulfur atoms in single crystals were found to play an important role in the solid-state spectra of the ethylenedithio derivative.

Tetrathiabenzoquinone derivatives, 2,3,7,8-tetrahydrobenzo[1,2-b:4,5-b′]bis[1,4]dithiin-5,10-dione ($C_{10}H_8O_2S_4$) (**1**) and 3,4,9,10-tetrahydro-2*H*,8*H*-benzo[1,2-b:4,5-b′]bis[1,4]dithiepin-6,12-dione ($C_{12}H_{12}O_2S_4$) (**2**), as shown in Scheme 1, are composed of the benzoquinone group as the chromophore and the sulfur atoms and the carbonyl groups as the donor and the acceptor, respectively. These dyes form a typical cross-conjugation system. They have attracted attention as a new organic pigment because of their poor solubility in various organic solvents as well as vivid coloration in the solid state.[1] **1** has also been known to exhibit a large third-order non-linear susceptibility.[2] **1** is characterized by an extremely large bathochromic shift of about 6612 cm^{-1} on going from a solution to the solid state. The displacement energy of the bathochromic shift upon crystallization depends considerably on the side-chain group, although no significant difference is recognized in their solution spectra. The bathochromic displacement of **2** (ca. 2101 cm^{-1}) corresponds to only about one-third of that of **1**. X-ray structure analyses have revealed that there are noticeable differences in the intermolecular distance and the intermolecular atomic contacts, although their crystal structures are nearly isomorphous.[3]



Scheme 1.

In this investigation, the electronic structures of two tetrathiabenzoquinone derivatives have been studied in order to interpret their solid-state spectra on the basis of the crystal structure. An understanding of the electronic structure in the solid state is of great importance for improving the physical properties, as mentioned above; also, the design of novel supramolecular systems[4] exhibit unusual properties in contrast to isolated molecular systems. The present study focused on intermolecular interactions in the solid state to elucidate the electronic structure. One of the typical intermolecular interactions in dyes and pigments is an exciton coupling effect,[5,6] which is an interaction between transition dipoles. The bathochromic shift on going from a solution to the solid state of conventional organic pigments, such as diketopyrrolopyrroles[7] and phthalocyaninatomagnesium compounds,[8] has been known to be mainly caused by this effect. In addition, the influence of the observed close atomic contacts in single crystals on the electronic state has also been investigated by molecular-orbital calculations.

Experimental

Sample Preparation. Both compounds **1** and **2** were prepared by reported procedures.[1,9] Single crystals of **1** and **2** were obtained by recrystallization from chloroform and chlorobenzene, respectively, as dark-colored prisms. Evaporated thin films were prepared using vacuum evaporation equipment (Tokyo Vacuum Co. Ltd., model EG240). Samples for measurements of the absorption spectra and X-ray diffraction were evaporated onto glass slides by about 1000 Å and 3000 Å, respectively. The phase transition of **1** was carried out by exposing to chlorobenzene vapor for several days.

Measurements. UV/vis spectra were recorded on a Shimadzu

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UV-2400PC spectrophotometer. Polarized reflection spectra were measured on single crystals of **1** and **2** by means of a UMSP 80 microscope-spectrophotometer (Carl Zeiss). An Epiplan Pol (× 8) objective was used together with a Nicol-type polarizer. The reflectivity was corrected relative to the reflection standard of silicon carbide. The X-ray diffraction of evaporated films was measured by a Rigaku RINT-2000 diffractometer using graphite-monochromated Cu $K\alpha$ radiation (λ = 1.5415 Å, 15 kW h^{-1}). The temperature dependence of the absorption spectra of evaporate films were measured in cryostat equipment (Iwatani Industrial Gases Corp., cold head: D105 and compressor: CW301) between 300 and 20 K.

Calculations. Electronic spectra were calculated using the INDO/S Hamiltonian in the ZINDO[10] program package. Calculations of the exciton coupling effects and an estimation of intermolecular interactions by the energy-partition method[11,12] were carried out as described below. All calculations were performed on a Power Macintosh 8500/120 computer.

(a) Exciton Coupling Effects.[5,6] Transition dipoles are induced on molecules as soon as the molecules are excited by light irradiation. Resonance interactions then occur between transition dipoles to displace the excited energy level downwards (bathochromic shift) or upwards (hypsochromic shift), depending on the relative orientation of the transition dipoles. This is an exciton coupling effect and is often quite significant in organic dyes and pigments because their absorption coefficients are extremely large. The present treatment has been employed in various molecular systems, such as molecular crystals or dye-aggregates: organic pigments[7,8] and J-aggregates of cyanine dyestuffs.[13] The exciton displacement energy ($\Delta E_{\mathrm{exciton}}$), which corresponds to the spectral shift, is given by $\Delta E_{\mathrm{exciton}} = |\mu|^2(1 - 3\cos^2\theta)/r^3$, where the transition moment is denoted by μ, and the distance and angle between two transition dipoles by r and θ, respectively. The transition moment (μ) is found by molecular-orbital calculations on the basis of X-ray x, y, z coordinate sets. The term $(1 - 3\cos^2\theta)/r^3$ determines the geometrical relationship of the transition moment, which is correlated with the crystal structure. The calculations were carried out on the nearest-neighbor molecules. Then, the total energy displacement was summed over the nearest neighbors in consideration of the number of equivalent molecules.

(b) Energy Partition Method.[11,12] Intermolecular interactions in the ground state can be roughly estimated by the energy-partition method using semi-empirical molecular orbital calculations. Because the corresponding molecular pair is regarded as a supramolecule and then their energy state was calculated[14] using the AM1[15] Hamiltonian in the MOPAC 6. X-ray coordinate sets were used. The calculated energy (E_{total}) can be divided into the one-center term (E_i) and the two-center term (E_{ij}). The two-center term is correlated with the bonding energy, although it is not exactly the same. This energy term is composed of the resonance energy (E_{res}), the exchange energy (E_{exc}) and the coulomb energy (E_{el}). Among them, the intermolecular E_{res} between non-hydrogen atoms was evaluated, since the resonance energy approximately corresponds to the covalent bond:

$$E_{\mathrm{total}} = \sum_{i} E_i + \sum_{i<j} E_{ij} \tag{1}$$

$$E_{ij} = E_{\mathrm{res}} + E_{\mathrm{exc}} + E_{\mathrm{el}} \tag{2}$$

Results

Solution and the Solid-State Spectra. Figure 1 shows the solution and the solid-state spectra of evaporated films of **1** and **2**. **1** reveals pale yellowish-green in solution (λ_{max} = 427 nm). However, the color changed to vivid red (λ_{max} = 526 nm) upon evaporation onto a slide glass. Furthermore, the color of evaporated **1** changed from vivid red to dull red (λ_{max} = 595 nm) upon exposing chlorobenzene vapor for several days. This color change was accompanied by a phase transition, as described in the next section. The color of **2** in solution was almost the same as that of **1** (λ_{max} = 450 nm); however, evaporated films of **2** were pale orange (λ_{max} = 497 nm). Evaporated films of **2** didn't undergo any color change upon exposure to various organic solvents. The bathochromic displacement on going from solution to the solid state in **1** after a vapor treatment was about 6621 cm^{-1}. This bathochromic shift was extremely large, compared to that of **2**, which was about 2101 cm^{-1}.

X-ray Diffraction. X-ray diffraction diagrams of evaporated **1** and **2** are illustrated in Fig. 2. **1** is highly ordered in evaporated films[16] to reveal a very intensive peak at around θ = 25° both before and after a vapor treatment. The interplanar distance is slightly contracted by a vapor treatment to give the remarkable spectral change shown in Fig. 1(a). The peak after a vapor treatment corresponds to the interplanar distance along

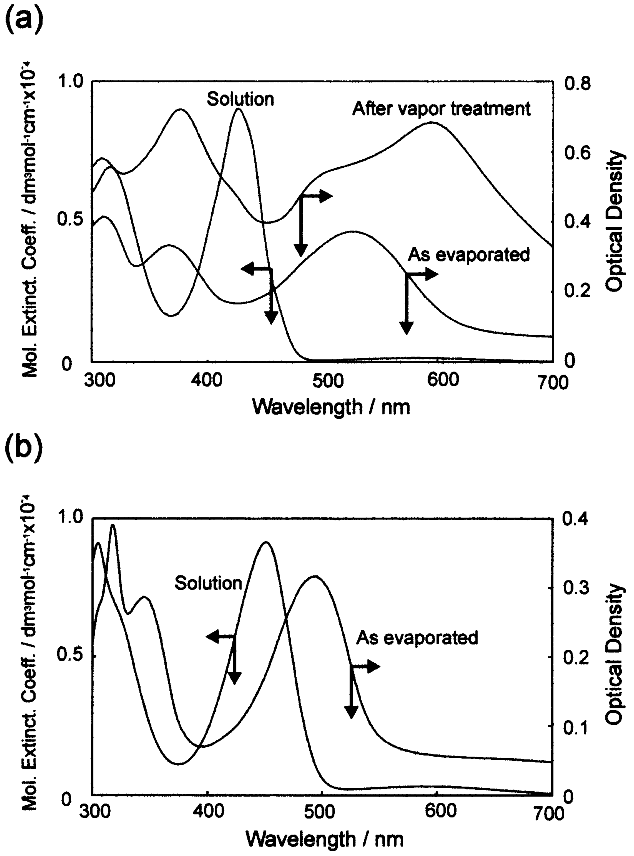

Fig. 1. Solution and the solid-state spectra of (a) **1** and (b) **2**.

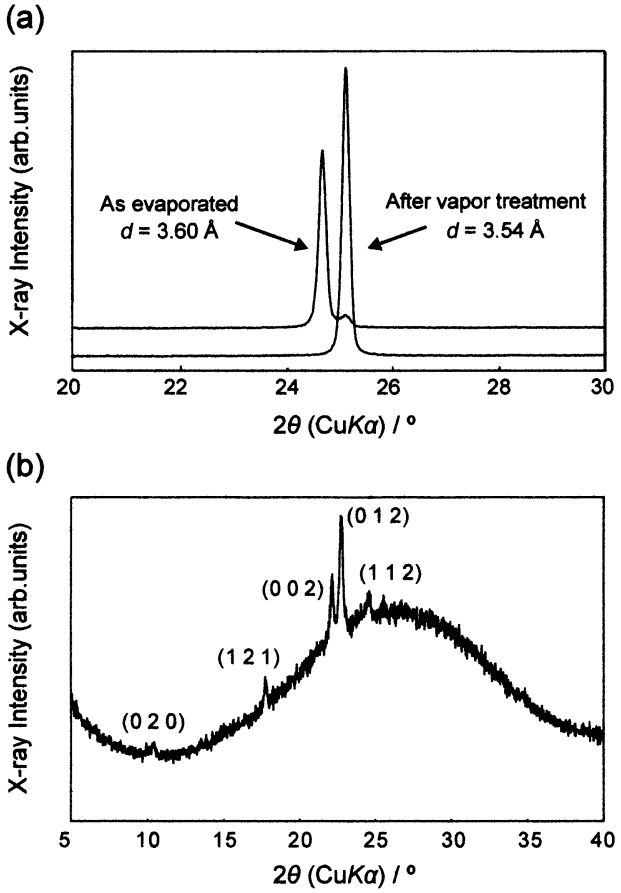

Fig. 2. X-ray diffraction diagram of evaporated (a) **1** and (b) **2**.

the stacking axis.[3] The phase of evaporated **2** was found to be the same as that of single crystals.

Crystal Structure of 1 and 2.[3] Their crystal structures are depicted in Fig. 3 projected onto the *ab* plane and the *bc* plane, respectively. The crystallographic parameters are listed in Table 1. In both compounds, the molecules are stacked along the *c*-axis alternatively twisted by about 80° to give a characteristic one-dimensional molecular column. The molecules of **1** are arranged on the same plane that is parallel to the *ab* plane; however, there is slight deviation between the neighboring columns along the [110] direction in **2**. Although their molecular arrangements are almost the same, there is a noticeable difference in the interplanar distance and the intermolecular atomic contact. The interplanar distances along the stacking axis are 3.59(2) Å for **1** and 3.98(9) Å for **2**, respectively. Very close atomic contact between sulfur atoms is observed along the *a*-axis (3.229(2) Å) in **1** as designated by the dotted ellipse (A) in Fig. 3(a). Furthermore, a relatively close S–S contact is also recognized between stacking molecules (3.6531(2) Å, dotted ellipse (B)). On the other hand, those in **2** are longer than those in **1** due to the effect of the side-chain group to enlarge the molecular volume.

Polarized Reflection Spectra. The polarized reflection spectra measured on single crystals of **1** and **2** are shown in Fig. 4 for polarization parallel and perpendicular to the stacking *c*-axis. In **1**, an intense and broad reflection band appears at around 590 nm for both polarizations. On the other hand, an intense and sharp reflection band was observed at around 520 nm only for polarization perpendicular to the *c*-axis in **2**. The calculated transition moment in the visible region appears on the molecular plane along the direction of the C=O bond in both compounds. Therefore, interactions between the transition moments would contribute to the bands observed for polarization perpendicular to the *c*-axis. On the other hand, the reflection band observed for polarization parallel to the *c*-axis in **1** cannot be interpreted in terms of interactions between the transition moments. It could be postulated that the present out-of-plane band is assigned to an intermolecular charge-transfer transition or an inter-band transition.

Exciton Coupling Effects. Table 2 lists the calculated results of exciton coupling effects. The calculations were carried out on 12 nearest neighbors around the molecule at (1/2, 0, 0) using the calculated transition dipole (μ = 1.197 Å) for **1**, and at (1/4, 1/4, 0) and μ = 1.224 Å for **2**, respectively. The minus and plus signs of energy displacement correspond to the bathochromic and the hypsochromic shifts, respectively. The calculated interactions in the excited state were found to contribute to a relatively small bathochromic shift in both compounds.

Energy Partition Method. The selected intermolecular resonance energies (E_{res}) between non-hydrogen atoms are listed in Table 3 together with the contact distances. A very large resonance energy was recognized between sulfur atoms in both the translational pair along the *a*-axis and the stacking pair in **1**. No other appreciable E_{res} between non-hydrogen atoms was observed. This result implies that the intermolecular overlap of the molecular orbital arises between the corresponding molecular pair to form a different energy state from that of the isolated molecule. On the other hand, no considerable E_{res} was obtained, except for that between sulfur atoms in the translational pair along the *a*-axis in **2**. The difference in both compounds is particularly remarkable in the stacking pair due to an effect of the side-chain group.

Temperature Dependence of Absorption Spectra. Figure 5(a) shows the temperature dependence of the absorption spectra of **1** before and after a vapor treatment. The spectral shift, depending on the temperature, is due to the contraction of a crystal lattice owing to the decrease of atomic thermal motion. Before a vapor treatment, the absorption maximum is significantly displaced towards the longer wavelength region, as compared to that of after a vapor treatment. This may be explained in the following way. Before a vapor treatment, the molecules are sparsely packed in comparison with those after a vapor treatment. The degree of lattice contraction is therefore more significant than that after a vapor treatment. Consequently, a large temperature dependence was observed before a vapor treatment. The temperature dependence in **2** is small, as depicted in Fig. 5(b).

Discussion

Phase Transition in 1. An additional spectral change oc-

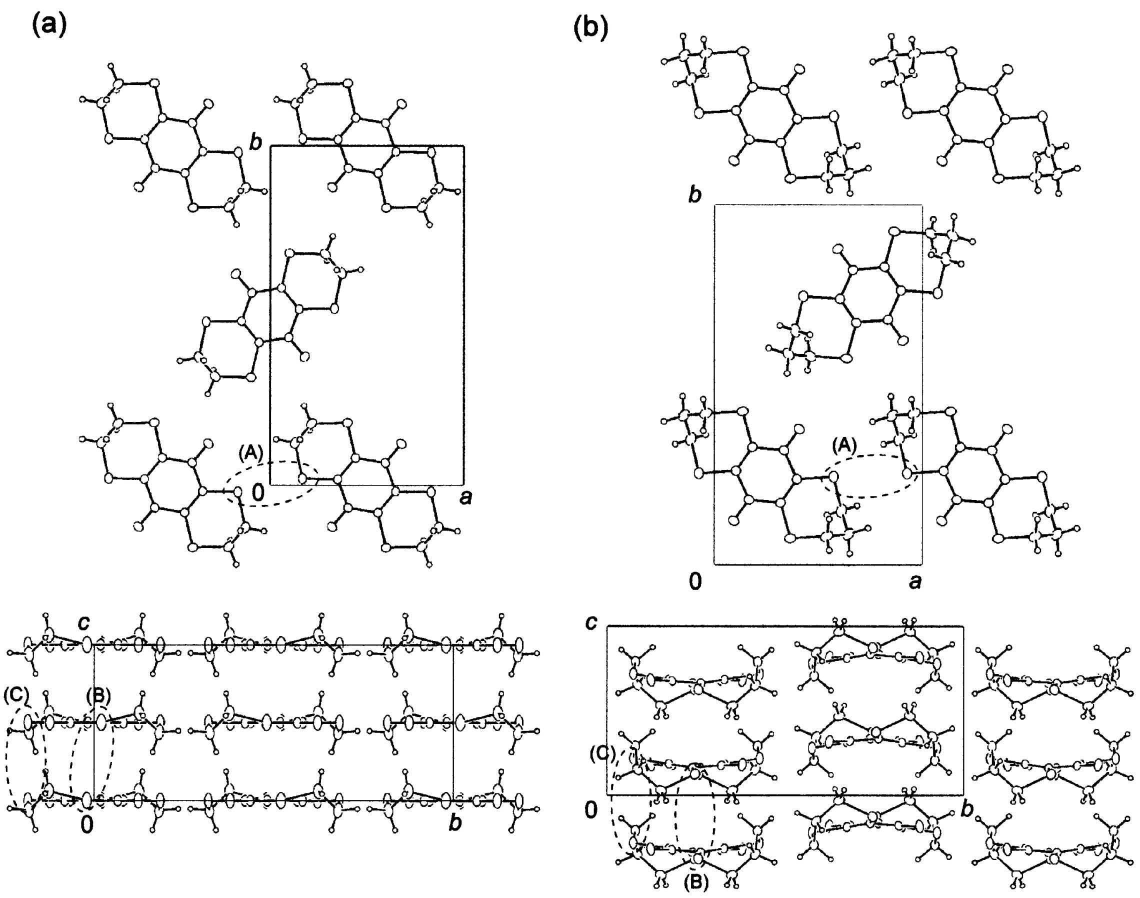

Fig. 3. Crystal structure of (a) **1** and (b) **2** projected onto the *ab* plane and the *bc* plane. (A), (B), and (C) indicate the calculated intermolecular atomic pair as shown in Table 3.

Table 1. Crystallographic Parameters

Compound	**1**	**2**
Formula	$C_{10}H_8O_2S_4$	$C_{12}H_{12}O_2S_4$
Crystal system	Orthorhombic	Orthorhombic
Space group	*Ibam*	*Pccn*
Z	4	4
Molecular weight	288.41	316.47
a/Å	9.441(2)	9.758(2)
b/Å	16.583(2)	16.846(2)
c/Å	7.184(3)	7.981(2)

curs in evaporated **1** by exposing an appropriate organic solvent, such as chlorobenzene. This spectral change is accompanied by a change in the interplanar distance. The interplanar distance after a vapor treatment is in good accordance with the [002] distance of single crystals of **1**. The absorption maximum at around 600 nm after a vapor treatment also agrees with those of the polarized reflection spectra measured on the single crystals. The phase after a vapor treatment is thus considered to be almost the same as that of single crystals. On the other hand, the phase as evaporated is regarded as a metastable phase, because the films as evaporated slowly undergo a phase transition, even under the ambient condition.

Exciton Coupling Effects in 1 and 2. The energy displacement based on exciton coupling effects (interactions between transition dipoles) is found to be relatively small in both compounds. The displacement energy of **1** is slightly larger than that of **2**. These results can be well understood based on their isomorphous molecular arrangement as well as the similar transition dipole length, in spite of the difference in their intermolecular distance. The temperature dependence of the absorption spectra of evaporated films of both compounds reveals that the influence of the intermolecular interaction on the optical absorption is relatively small. The lattice contraction of single crystals, depending on the temperature, indicates that a considerable contraction occurs along the stacking *c*-axis; also, the degree of contraction is almost the same in both compounds.[17] These experimental results are consistent with the small contribution of the exciton coupling effect on the optical absorption.

The polarized reflection spectra of single crystals of **2** exhibit an intense and sharp reflection band, which is in good accordance with that of evaporated films, only for polarization parallel to the transition moment. Consequently, the bathochromic shift on crystallization in **2** is qualitatively ascribed to the present interaction in the excited state. However, a broad reflection band is recognized for both polarization directions in

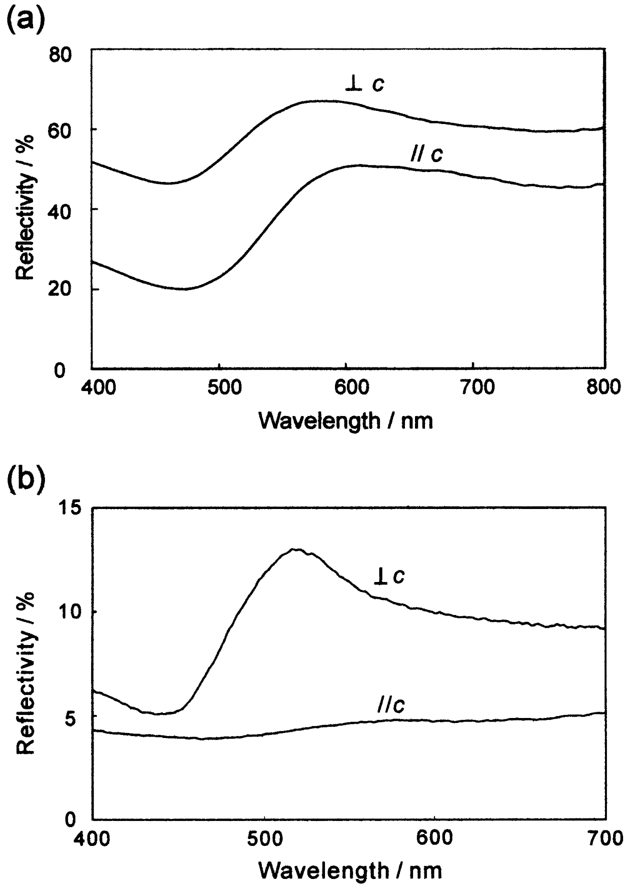

Fig. 4. Polarized reflection spectra measured on single crystals of (a) **1** and (b) **2**.

Table 2. Calculated Energy Displacement for (a) **1** and (b) **2**. The Molecular Sites are Designated in Fractional Coordinates

(a)

Site	Number of molecules	r/Å	θ/°	ΔE/cm^{-1}
(3/2, 0, 0)	2	9.44	50.27	−49
(1/2, 1, 0)	2	16.58	39.73	−31
(1, 1/2, 1/2)	4	10.20	22.86	−267
(0, 1/2, 1/2)	4	10.20	70.76	116
Total	12			−762

μ = 1.197/Å

(b)

Site	Number of molecules	r/Å	θ/°	ΔE/cm^{-1}
(5/4, 1/4, 0)	2	9.758	54.48	−2
(1/4, 5/4, 0)	2	16.846	35.52	−36
(3/4, 3/4, 0)	2	10.160	17.50	−286
(3/4, −1/4, 0)	2	10.160	66.69	88
(3/4, 3/4, 1)	2	10.975	28.00	−176
(3/4, −1/4, 1)	2	10.975	68.51	78
Total	12			−667

μ = 1.224/Å

Table 3. Selected Intermolecular E_{res} for **1** and **2**

Compound	Atom-pair	Contact distance/Å	E_{res}/eV
1	S–S (A)	3.229	−0.1957
	S–S (B)	3.653	−0.0225
	S–S (C)	4.059	−0.0069
2	S–S (A)	3.455	−0.0886
	S–S (B)	3.994	−0.0052
	S–S (C)	4.575	−0.0013

1, even for polarization perpendicular to the transition moment. This spectrum together with the large bathochromic displacement cannot be interpreted in terms of the present small exciton coupling effects. Other intermolecular interactions must be taken into consideration in order to explain the spectral change in **1**.

Mechanism of Bathochromic Shift of 1. As described in the previous section, the polarized reflection spectra of **1** indicate that other intermolecular interactions influence the solid-state spectra in addition to the exciton coupling effects. The change in the absorption spectra as well as the interplanar distance accompanied by the phase transition in evaporated **1** suggests that a new absorption band at around 600 nm appears due to a slight contraction in the interplanar distance. The temperature dependence of the absorption spectra of as evaporated **1** also indicates that the large bathochromic shift results from lattice contraction. These results also cannot be interpreted only in terms of the present small exciton coupling effects.

An out-of-plane reflection band in the visible region observed along the stacking axis could be ascribed to a charge-transfer band. However, the charge-transfer transition between homo-molecules is hardly considered to exhibit such an intense optical transition.[18,19] Only a few examples have been known.[20–22] We have thus assumed that the out-of plane band can be ascribed to an inter-band transition from the viewpoint of the very broad band shape. In general, close van der Waals atomic contacts between chalcogen atoms, such as sulfur, selenium, and tellurium, have been known to play a decisive role in the electronic properties of various organic semi-conductors and superconductors.[23–26] A band structure is known to form by means of the several close atomic contacts between chalcogen atoms to exhibit extraordinary electronic properties. We have thus focused on the close S–S atomic contacts. The energy partition method enables us to roughly estimate the influence of atomic contacts on the electronic state. The most significant difference in the calculated result of E_{res} is recognized between sulfur atoms in the stacking pair. Those of **1** are about five-times as large as those of **2**, which correspond to the intermolecular E_{res} between non-hydrogen atoms without contact. The contraction along the stacking axis is found to be responsible for the spectral change from the result of the phase transition as well as the temperature dependence. In **1**, therefore, strong S–S interactions have arisen along the stacking axis in addition to the *a*-axis to form an energy band that results in the extremely

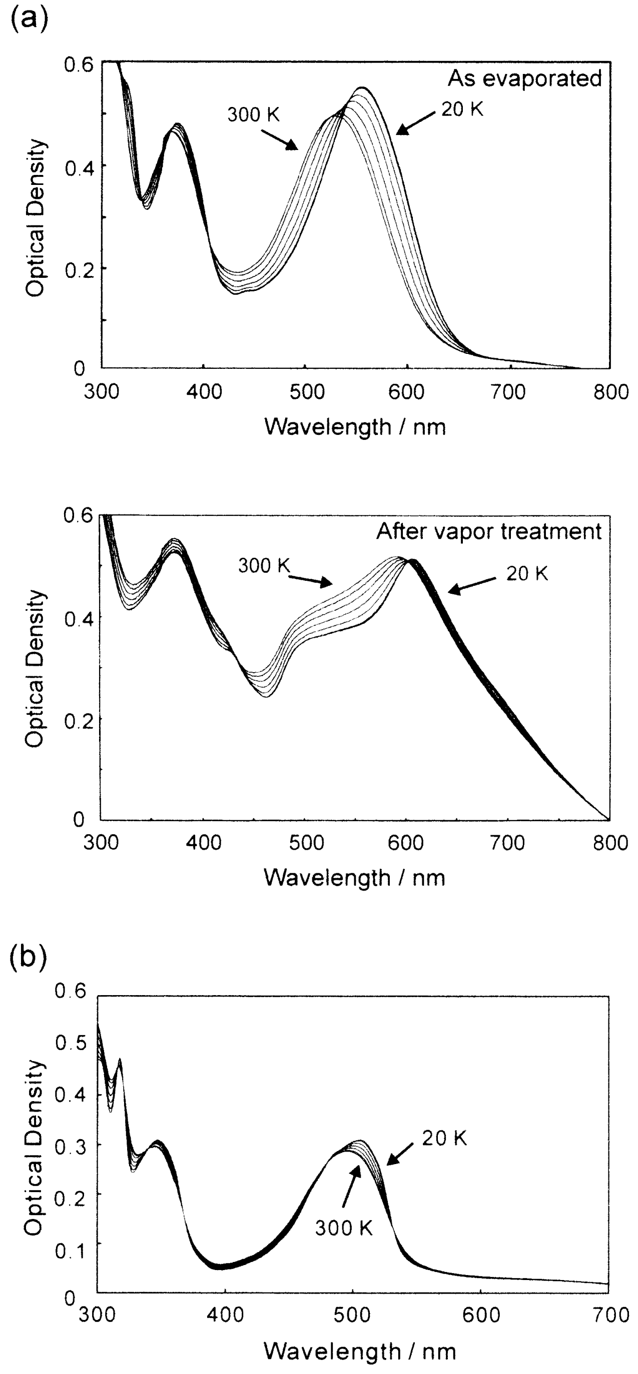

Fig. 5. Temperature dependence of the absorption spectra of evaporated (a) **1** and (b) **2**.

large bathochromic shift upon crystallization together with the out-of-plane reflection band observed in the single crystals. This is in good accordance with the experimental results of the evaporated films. Judging from the optical properties and the calculated results, we have concluded that the major interaction influencing the electronic state in the solid state of **1** is the present S–S interaction.

Conclusions

Tetrathiabenzoquinone derivatives crystallize in the characteristic molecular arrangement consists of a one-dimensional column and a two-dimensional sheet. Intermolecular interactions in the excited state, depending on the molecular arrangement in single crystals, exciton coupling effects, are found to be relatively small. The small bathochromic shift on crystallization of **2** is attributed to this interaction. However, an extremely large bathochromic shift of **1** could be considered to arise from the formation of the band structure due to strong interactions between intermolecular sulfur atoms. The out-of-plane reflection band in single crystals could also be well understood. However, we need further investigations on the electronic properties and calculations of a band structure in order to clarify the detailed electronic structure of **1**.

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References

1 K. Takagi, A. Mizuno, A. Iwamoto, M. Furusyo, and M. Matsuoka, *Dyes Pigm.*, **36**, 35 (1998).

2 M. Matsuoka, A. Oshida, A. Mizoguchi, Y. Hattori, and A. Nishimura, *Nonlinear Optics*, **10**, 109 (1995).

3 S. Matsumoto and J. Mizuguchi, *Acta Crystallogr. Sect. B*, in press.

4 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, **34**, 2311 (1995).

5 M. Kasha, *Radiat. Res.*, **20**, 55 (1963).

6 M. Kasha, "Spectroscopy of the Excited State," Plenum Press, New York (1976).

7 J. Mizuguchi, *J. Phys. Chem. A*, **104**, 1817 (1999).

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

9 T. Otsubo, K. Nobuhara, K. Kanefuji, Y. Aso, and F. Ogura, *J. Phys. Org. Chem.*, **1**, 275 (1998).

10 ZINDO: M. C. Zerner, "A General Semiempirical Program Package," Department of Chemistry, University of Florida, Gainesville, FL.

11 T. Hirano and E. Osawa, *Croatica Chem. Acta*, **57**, 1633 (1984).

12 H. Koinuma, M. Funabashi, K. Kishio, M. Kawasaki, T. Hirano, and K. Fueki, *Jpn. J. Appl. Phys.*, **25**, 1811 (1986).

13 A. P. Marchetti, C. D. Salzberg, and I. P. Walker, *J. Chem. Phys.*, **64**, 4693 (1976).

14 J. Mizuguchi, *Denshi Shashin*, **37**, 67 (1998).

15 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

16 K. Yoshida, M. Tsujimoto, S. Isoda, T. Kobayashi, T. Kamata, and M. Matsuoka, *Mol. Cryst. Liq. Cryst.*, **322**, 161 (1998).

17 S. Matsumoto, unpublished result.

18 M. Pope and C. E. Swenberg, "Electronic Processes in Organic Crystals," Clarendon Press, Oxford (1982).

19 J. J. Ewing and D. R. Kearns, *J. Chem. Phys.*, **44**, 3139 (1966).

20 J. Tanaka and M. Shibata, *Bull. Chem. Soc. Jpn.*, **41**, 34 (1968).

21 S. C. Abbi and D. M. Hanson, *J. Chem. Phys.*, **60**, 319 (1974).

22 N. Sano and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **59**, 843 (1986).

23 P. C. W. Leung, T. J. Emge, M. A. Beno, H. H. Wang, J. M. Williams, V. Petricek, and P. Coppens, *J. Am. Chem. Soc.*, **107**, 6184 (1985).

24 A. J. Schultz, H. H. Wang, M. Williams, and A. Filhol, *J. Am. Chem. Soc.*, **108**, 7853 (1986).

25 Y. Yamashita, S. Tanaka, K. Imaeda, and H. Inokuchi, *Chem. Lett.*, **1991**, 1213.

26 Y. Yamashita, S. Tanaka, K. Imaeda, H. Inokuchi, and M. Sano, *J. Org. Chem.*, **57**, 5517 (1992).