The Reflection Spectra of the Crystalline Electron Donor-Acceptor Complexes of TCNQ

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The polarized reflection spectra were measured on the crystals of TCNQ complexes with phenothiazine, anthracene, pyrene, acenaphthene, carbazole, hexamethylbenzene, and 1,10-phenanthroline. The crystalline absorption spectra were obtained by the K-K transformation of the reflection spectra. The charge-transfer degree and the stabilization energy in the ground state were estimated for each complex by analysing the charge-transfer bands in the solid state. The charge-transfer degree of the TCNQ–phenothiazine complex is 19.6%, while those of the TCNQ–carbazole, anthracene, and hexamethylbenzene complexes are 12.0, 10.5, and 8.0% respectively. Furthermore, those values for TCNQ–1,10-phenanthroline, acenaphthene, and pyrene are about 5%. The relationship between the charge-transfer excitation energy and the ionization potential of a series of the donor molecules is also discussed.

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a strong electron-acceptor and forms molecular complexes with various electron donors. Investigation has been carried out extensively to elucidate the nature of the intermolecular interaction in these molecular complexes. The appearance of the charge-transfer (CT) band, absent from the constituent free molecules, is characteristic of these complexes; the correlation of the electronic states of the complexes with the absolute absorption intensity of the CT band was discussed by Tanaka.[1] That is, the charge-transfer degree in the ground state can be obtained by measuring the absorption intensity of the CT band; it can thus be found to what extent the charge-transfer structures contribute to the stabilization of the electron donor-acceptor complex in the ground state.

In this paper, the author will present the crystal reflection spectra of TCNQ complexes with phenothiazine, anthracene, pyrene, acenaphthene, carbazole, hexamethylbenzene, and 1,10-phenanthroline. These reflection spectra will then be transformed into the absorption spectra by the Kramers-Kronig (K-K) method. The transformed absorption spectra will enable us to discuss the charge-transfer degrees of a series of complexes with a common acceptor (TCNQ) and the stabilization energies in the ground state.

Experimental

Single crystals of TCNQ complexes were crystallized after hot euimolar solutions of the components had been mixed and allowed to cool very slowly.

The reflection spectra at the normal incidence have been measured over the range of 5000—40000 cm^{-1} by means of a reflection spectrophotometer made in our laboratory, while the absorption spectra have been obtained by the K-K transformation. The oscillator strength along the α axis of the crystal may be evaluated by using the following equation,

$$f^{\alpha} = 4.32\times10^{-9}\int n_{\alpha}(\sigma)\varepsilon_{\alpha}(\sigma)\mathrm{d}\sigma,$$

where the integration is effected over the whole band, where σ is the wavenumber, and where n_{α} and ε_{α} are the α components of the refractive index and the molar absorption coefficient.

Theoretical

The analysis of the electronic states of the CT complexes was discussed by Tanaka[1] and so will be only briefly summarized here.

TCNQ complexes form a configuration of the ADA type in the crystal. Then, the ground state can be described by a wavefunction,

$$\Psi_0 \simeq \Phi(\mathrm{ADA}) + \sum_i b_i\{\Phi_i(\mathrm{AD^+A^-}) + \Phi_i(\mathrm{A^-D^+A})\}/\sqrt{2},$$

where $\Phi(\mathrm{ADA})$ represents a non-bonding, and $\Phi_i(\mathrm{AD^+A^-})$ and $\Phi_i(\mathrm{A^-D^+A})$, the i-th CT configurations. The charge-transfer degree and the stabilization energy in the ground state are given as $\sum_i b_i^2$ and $\Delta E=\sum_i b_i^2 E_{\mathrm{CT}}^i$. The wavefunction $\Psi_{\mathrm{CT}}^i(-)$ for the optically allowed i-th excited state is given by

$$\Psi_{\mathrm{CT}}^i(-) \simeq \{\Phi_i(\mathrm{AD^+A^-}) - \Phi_i(\mathrm{A^-D^+A})\}/\sqrt{2},$$

and the oscillator strength is defined as follows:

$$f_i = 3\times1.085\times10^{11}E_{\mathrm{CT}}^i b_i^2|\boldsymbol{R}_{\mathrm{AD}}|^2,$$

where $\boldsymbol{R}_{\mathrm{AD}}$ is the vector between the acceptor and donor molecules in units of cm and E_{CT}^i is the excitation energy in cm^{-1}. Accordingly, by comparing the experimental and theoretical oscillator strengths, we can obtain the magnitude values of b_i^2 and also information about the electronic states of the CT complexes.

The b_i coefficient can be correlated to the so-called transfer integral, $t_{Ak,Dl}$, as follows:

$$\begin{aligned} b_i &= \sqrt{2}\,(\Phi(\mathrm{ADA})|H|\Phi_i(\mathrm{AD^+A^-}))/E_{\mathrm{CT}}^i, \\ &= 2(\phi_{\mathrm{A}}^k|F|\phi_{\mathrm{D}}^l)/E_{\mathrm{CT}}^i, \\ &\equiv 2t_{Ak,Dl}/E_{\mathrm{CT}}^i, \end{aligned}$$

where $\phi_{\mathrm{A}}{}^k$ is the k-th molecular unoccupied orbital of the acceptor, and $\phi_{\mathrm{D}}{}^l$, the l-th molecular occupied orbital of the donor. The transfer integral, $t_{Ak,Dl}$, may be approximated by the use of the overlap integral, $S_{Ak,Dl}$

$$t_{Ak,Dl} = -KS_{Ak,Dl} = -K(\phi_{\mathrm{A}}^k|\phi_{\mathrm{D}}^l).$$

Here, K is the constant taken as 15.0 eV and the overlap integral can be estimated by a method shown before.[2] Therefore, the comparison between the observed and calculated values of b_i^2 makes it possible to assign the character of the CT band. The molecular orbital is represented by taking the long axis of the molecule

as the y axis and the short axis as the z axis, except in the case of the hexamethylbenzene molecule. In hexamethylbenzene, the z axis is taken as the normal to the molecular plane.

All of the above-mentioned computations were carried out on a FACOM 230-75 computer at the Nagoya University Computation Center.

Results

TCNQ-Phenothiazine Complex. The complex of TCNQ-phenothiazine crystallizes in the form of needles elongated along the a axis, and the space group is C2/c.[3] TCNQ and phenothiazine molecules are stacked alternately in infinite columns parallel to the a axis. The interplanar distance is 3.44 A, and the distance between centers parallel to the a axis, R_{AD}, is 3.52 A. The mode of overlapping is shown in Fig. 1. The

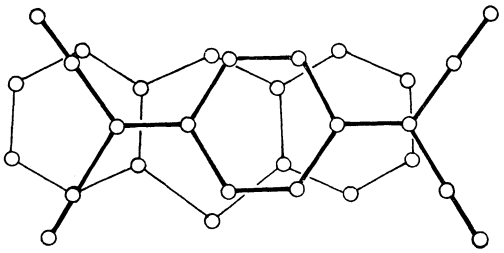

Fig. 1. The molecular overlap of the TCNQ-phenothiazine complex.

reflection spectra are observed for the polarizations parallel and perpendicular to the a axis on the (010) face, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 2 and 3.

The a-axis reflection spectrum shows three separate bands. The first band peak occurs at 6200 cm^{-1}, with a reflectivity of 31.6%, while the second peak occurs at 17800 cm^{-1}, with 6.6% reflectivity. The third band, in the region of 29000 cm^{-1}, has a reflectivity of 6.9%. The $a_\perp$ spectrum for (010) shows no clear structure in the region of the first a axis band at 6200 cm^{-1}. The

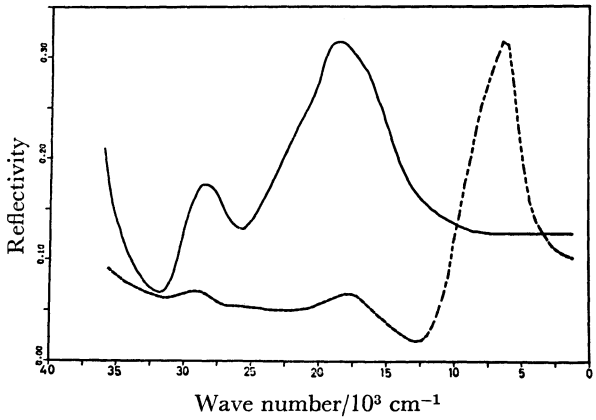

Fig. 2. The a(dashed line) and $a_\perp$(solid line) axes reflection spectra obtained on the (010) face of the crystal of TCNQ-phenothiazine complex.

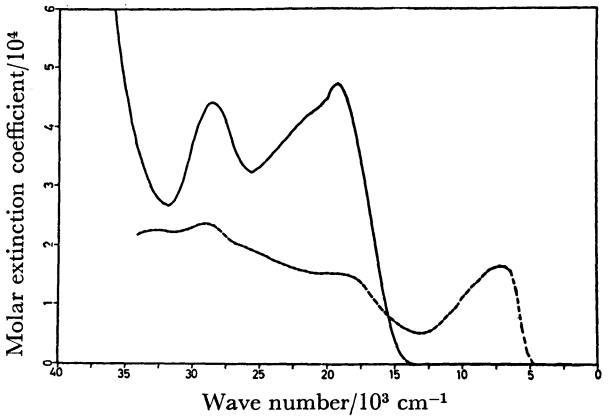

Fig. 3. The a(dashed line) and $a_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ-phenothiazine complex.

intense band at 18500 cm^{-1} has a reflectivity of 31.5%, and the 28400 cm^{-1} band has a 17.4% reflectivity.

In the absorption spectra, the 6200 cm^{-1} band is exclusively polarized along the a axis and can be

TABLE 1. THE CT TRANSITION ENERGIES (E_{CT} IN 10^3 cm^{-1}), THE CHRGE-TRANSFER DEGREES (b_i^2 IN %), AND THE STABILIZATION ENERGIES (ΔE IN kcal) IN THE GROUND STATE OF THE CRYSTALS OF TCNQ COMPLEXES

Donors	E_{CT}	I_p(eV)[17]	C(eV)	P(eV)	I_c(eV)[17]	Obsd			Calcd		ΔE
						f_i	R_{AD}(A)	b_i^2	$S_{Ak,Dl}$	b_i^2	
Phenothiazine	7.1	7.14	2.36	1.10	4.36	0.549	3.52	19.2	0.0121	17.0	3.89
Anthracene	12.8	7.4	2.32	0.69	5.6	0.189	3.50	3.7	0	0.0	1.34
	21.4					0.583	3.50	6.8	0.0190	4.6	4.16
(total)								(10.5)		(4.6)	(5.50)
Pyrene	13.2	7.55	2.28	0.83	5.8	0.212	3.57	3.9	0.0072	1.7	1.46
	19.5					0.091	3.57	1.1	{0.0051 / 0.0039}	{0.4 / 0.2}	0.61
(total)								(5.0)		(2.3)	(2.07)
Acenaphthene	14.3	7.66	2.36	0.73		0.271	3.37	5.1	0.0123	4.3	2.04
Carbazole	14.6		2.40			0.637	3.34	12.0	0.0246	16.6	5.00
Hexamethylbenzene	16.0	7.85	2.30	0.77		0.765	4.28	8.0	0.0163	6.1	3.66
1,10-Phenanthroline	20.5		2.34			0.407	3.41	5.2	0.0078	0.8	3.06

assigned to the CT transition from the highest occupied orbital ($\phi_D^8(b_1)$) of the phenothiazine molecule to the lowest unoccupied orbital ($\phi_A^9(b_{1g})$) of the TCNQ molecule. The oscillator strength of this band is 0.549, and the observed charge-transfer degree (19.2%) is in good agreement with the calculated value of 17.0%, as is shown in Table 1. The 18500 and 29000 cm^{-1} bands are strongly polarized along the $a_\perp$ axis. The inclination of the long axis of the molecule with respect to the stacking a axis is 75° on the (010) face, and the long-axis transitions of the TCNQ and phenothiazine molecules should be more intensely observed in the $a_\perp$ axis spectrum. Therefore, the 18500 cm^{-1} band may be regarded as due to the long-axis transition (LE_1) of the TCNQ molecule,[4] and the 29000 cm^{-1} band, as due to the long-axis transition of the phenothiazine molecule. The LE_1 band of TCNQ is 6400 cm^{-1} red-shifted from the peak occurring at 24900 cm^{-1} in the chloroform-solution spectrum. This large shift seems to be due to the large charge-transfer degree (*ca.* 19%) in the ground state of the crystal of the TCNQ-phenothiazine complex. The 29000 cm^{-1} band corresponds to the 31300 cm^{-1} band of the phenothiazine molecule in the ehtanol solution.

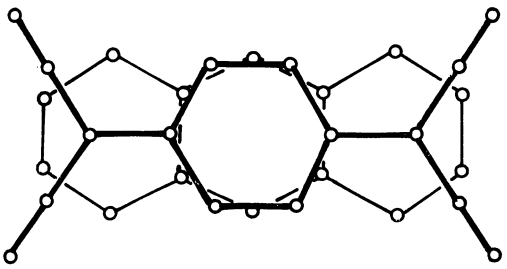

Fig. 4. The molecular overlap of the TCNQ–anthracene complex.

TCNQ–Anthracene Complex. The complex of TCNQ–anthracene forms a monoclinic crystal with a space group of C2/m,[5] and the structure consists of infinite columns of alternate TCNQ and anthracene molecules stacked in columns parallel to the c axis of the unit cell, with the mean molecular planes perpendicular to this axis. The mode of molecular overlap is such that the long axes of each molecule are parallel and their centers are superimposed, as is shown in Fig. 4. Therefore, the interplanar distance takes the same value (3.50A) as the intermolecular distance, R_{AD}. The reflection spectra are observed for the polarizations parallel and perpendicular to the c axis on the (010) face, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 5 and 6. These spectra coincide with the spectra measured by Eckhardt and Pennelly.[6]

The c-axis reflection spectrum shows two bands. The first band, at 11800 cm^{-1}, has a reflectivity of 7.3%, while the second band occurs at 20800 cm^{-1}, with a 5.3% reflectivity. The $c_\perp$ spectrum for (010) consists of one intense peak at 23200 cm^{-1} and one shoulder at 35300 cm^{-1}. The 23200 cm^{-1} band has a reflectivity of 35.6%.

In the absorption spectra, as there is no mixing between the CT band and the locally excited $\pi\rightarrow\pi^*$

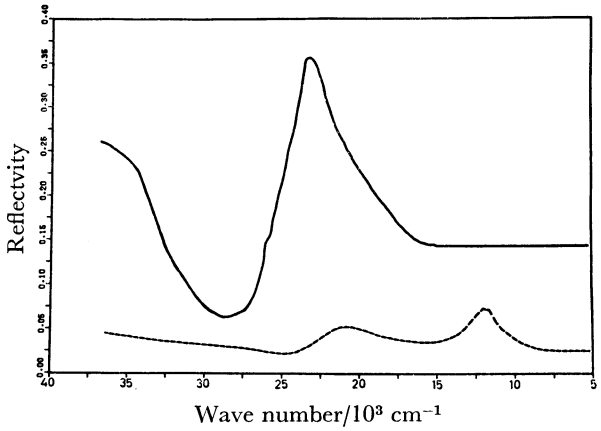

Fig. 5. The c(dashed line) and $c_\perp$(solid line) axes reflection spectra obtained on the (010) face of the crystal of TCNQ–anthracene complex.

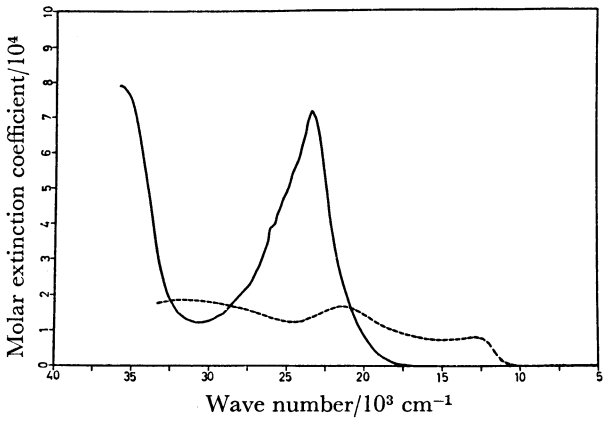

Fig. 6. The c(dashed line) and $c_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ–anthracene complex.

bands of each molecule in the complex with a D_{2h} symmetry, the c-axis polarized band can be assigned to the charge-transfer band. Therefore, the two CT bands are observed at 12800 and 21400 cm^{-1}; it should be noted that the second CT band, at 21400 cm^{-1}, becomes more intense than the first CT band, at 12800 cm^{-1}. The oscillator strengths of these CT bands are 0.189 and 0.583, and the contributions (b_i^2) to the charge-transfer degree in the ground state are 3.7 and 6.8% respectively. According to the molecular overlap shown in Fig. 4 and the overlap integrals given in Table 1, the transition from the highest occupied anthracene orbital ($\phi_D^7(b_{2g})$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$) is forbidden, but the CT transition can be allowed from the third occupied anthracene orbital ($\phi_D^5(b_{1g})$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$). Accordingly, the weak CT band at 12800 cm^{-1} may be assigned to the $\phi_D^7(b_{2g})\rightarrow\phi_A^9(b_{1g}$ transition, and the intense CT band at 21400 cm^{-1}, to the $\phi_D^5(b_{1g})\rightarrow\phi_A^9(b_{1g})$ transition. The calculated charge-transfer degree supports these assignments strongly, as is shown in Table 1. The $c_\perp$ absorption spectrum has two intense bands. The first band, at 23400 cm^{-1}

corresponds to the LE_1 band of the TCNQ molecule and the second band, in the region of 35000 cm^{-1}, to the β band of the anthracene molecule, which is polarized along the long axis of the anthracene molecule.[7]

TCNQ-Pyrene Complex. The crystal of the TCNQ-pyrene complex was obtained as very dark green needles by the slow evaporation of a tetrahydrofuran solution; the space group is $P2_1/b$.[8] The crystal structure is built up from isolated TCNQ and pyrene molecules alternating in plane-to-plane stacks, and the stacking axis is the crystalline a axis (the needle axis).

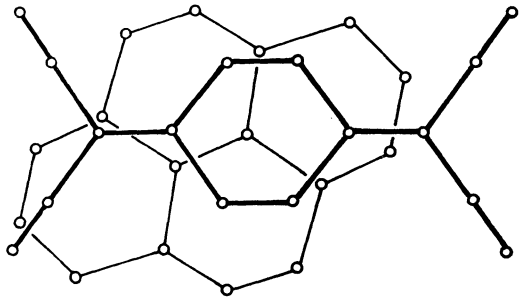

Fig. 7. The molecular overlap of the TCNQ-pyrene complex.

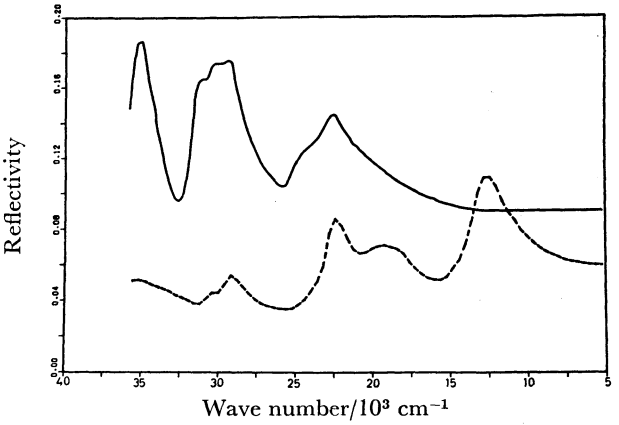

Fig. 8. The a(dashed line) and $a_\perp$(solid line) axes reflection spectra obtained on the (011) face of the crystal of TCNQ-pyrene complex.

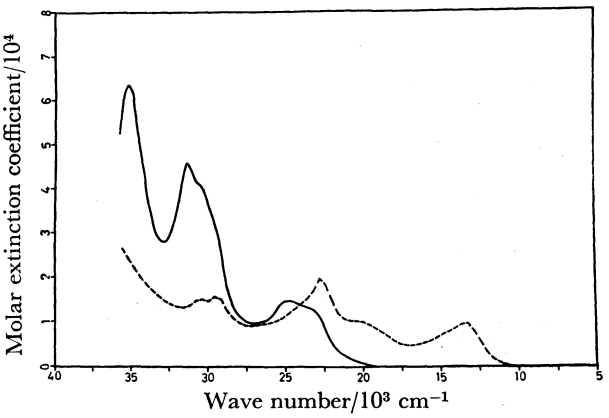

Fig. 9. The a(dashed line) and $a_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ-pyrene complex.

The mean perpendicular separation between the planes of adjacent donor and acceptor components is 3.50 A, and the intermolecular distance along the stacking axis, R_{AD}, is 3.57 A. The molecular overlap, as viewed in the direction perpendicular to the mean molecular planes, is shown in Fig. 7. The reflection spectra are observed for the polarizations parallel and perpendicular to the a axis on the (011) face, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 8 and 9.

The a axis reflection spectrum has five bands at 12600, 19300, 22400, 29200, and 35200 cm^{-1}. The reflectivity of the first band at 12600 cm^{-1} is 10.9%, while the broad second band at 19300 cm^{-1} has its reflectivity of 7.1%. The third band occurs at 22400 cm^{-1}, with an 8.6% reflectivity; the higher energy bands have lower reflectivities. The $a_\perp$-axis reflection spectrum shows no clear structure in the region of the first two bands in the a-axis spectrum. The first peak appears at 22400 cm^{-1}, with a reflectivity of 14.4%, while the 29400 and 35000 cm^{-1} bands have reflectivities of 17.5 and 18.7% respectively.

In the absorption spectra, the two bands at 13200 and 19500 cm^{-1} are active for the light polarized parallel to the a axis and may reasonably be assigned to the CT bands. The oscillator strengths of these two bands are 0.212 and 0.091, and the contributions (b_i^2) to the charge-transfer degree in the ground state are 3.9 and 1.1% respectively. Judging from the overlap integrals shown in Table 1, the first CT band seems to be due to the transition from the highest occupied pyrene orbital ($\phi_D^8(b_{2g})$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$), while the second CT band consists of nearly degenerate transitions from the third and fourth highest occupied pyrene orbital ($\phi_D^6(b_{3u})$ and $\phi_D^5(a_u)$). The third band, in the region of 24000 cm^{-1}, has the same magnitude as the absorption intensities in the a- and $a_\perp$-axes spectra. The (011) projection shows that the long axis of the TCNQ molecule is at an angle of 55° to the a axis, and the absorption intensities of the LE_1 band must be comparable for the a- and $a_\perp$-axes spectra. Therefore, the 24000 cm^{-1} band may be assigned to the LE_1 band of the TCNQ molecule. On the other hand, the long axis of the pyrene molecule is at an angle of 78° to the a axis, and the higher energy bands at 31400 and 35200 cm^{-1} should have stronger absorption intensities in the $a_\perp$-axis spectrum than in the a-axis spectrum. Therefore, the 31400 and 35200 cm^{-1} bands

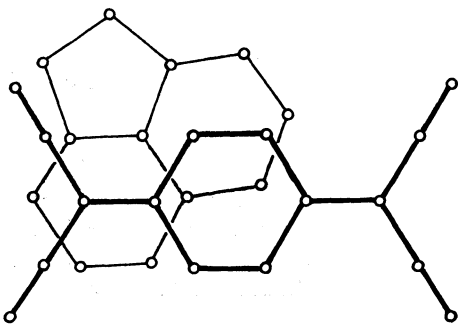

Fig. 10. The molecular overlap of the TCNQ-acenaphthene complex.

may be attributed to the long-axis transitions (p and β bands of the pyrene molecule[9]) respectively).

TCNQ-Acenaphthene Complex. The complex of TCNQ-acenaphthene forms a triclinic crystal of a space group of $P\bar{1}$,[10] and TCNQ and acenaphthene are stacked alternately in infinite columns parallel to the a-axis. The intermolecular distance along the stacking axis, R_{AD}, is 3.37 A, and the molecular overlap is as is depicted in Fig. 10. The reflection spectra are observed for the polarizations parallel and perpendicular to the a-axis on the (011) face, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 11 and 12.

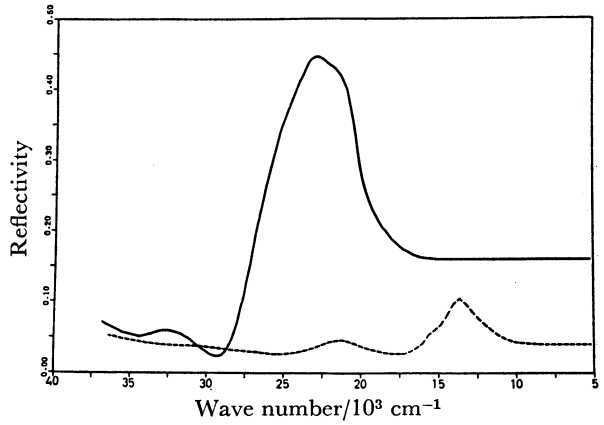

Fig. 11. The a(dashed line) and $a_\perp$(solid line) axes reflection spectra obtained on the (011) face of the crystal of TCNQ-acenaphthene complex.

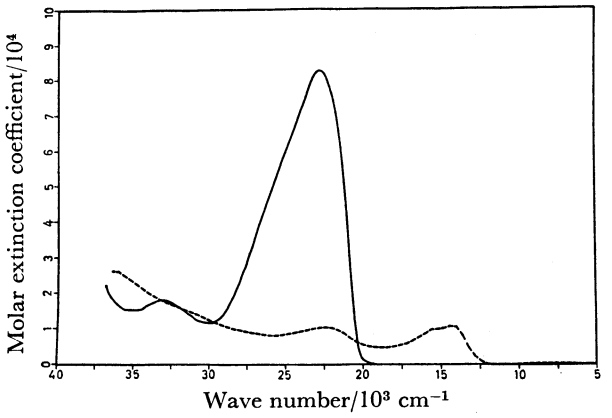

Fig. 12. The a(dashed line) and $a_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ-acenaphthene complex.

The a-axis reflection spectrum shows two separate bands. The first band peak occurs at 13600 cm^{-1}, with a reflectivity of 10.4%, and the second band appears at 21200 cm^{-1}, with a 4.6% reflectivity. The $a_\perp$-axis reflection spectrum shows no clear structure in the first a-axis band. The intense band occurs at 23000 cm^{-1}, with a reflectivity of 44.6%, and the weak band, at 32600 cm^{-1}, with a 6.0% reflectivity.

In the absorption spectra, the first band at 14300 cm^{-1} is active for the light parallel to the a axis and may be due to the CT transition from the highest occupied acenaphthene orbital ($\phi_D{}^5(a_2)$) to the lowest unoccupied TCNQ orbital ($\phi_A{}^9(b_{1g})$). The oscillator strength of the band is 0.271, and the charge-transfer degree in the ground state is 5.1%, as is shown in Table 1. The second band, at 22800 cm^{-1}, is more strongly polarized along the $a_\perp$-axis direction than alone the a axis. The inclination of the long axis of the molecule with respect to the stacking a axis is 85°, and the long-axis transitions of the TCNQ and acenaphthene molecules should be more intensely observed in the $a_\perp$-axis spectrum than in the a-axis. Therefore, the second band may be regarded as the LE_1 band of the TCNQ molecule. The third weak band, in the region of 33000 cm^{-1}, can be assigned to the α band of the acenaphthene molecule.[11]

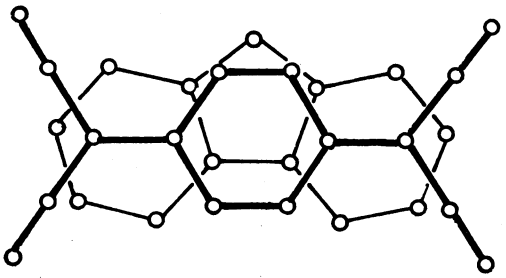

Fig. 13. The molecular overlap of the TCNQ-carbazole complex.

TCNQ-Carbazole Complex. The crystals of the TCNQ-carbazole complex are orthorhombic, and the space group is Immm.[12] The structure consists of infinite columns of alternate TCNQ and carbazole molecules, and the column is parallel to the c-axis. The molecular planes are perpendicular to the c-axis, and the long axes of each molecule are parallel to the a-axis. The molecular overlap is shown in Fig. 13. The intermolecular distance, R_{AD}, is the same as the mean perpendicular separation (3.34 A) between the molecular planes. The reflection spectra are observed for the polarizations parallel and perpendicular to the c-axis on the (010) face, and the absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 14 and 15.

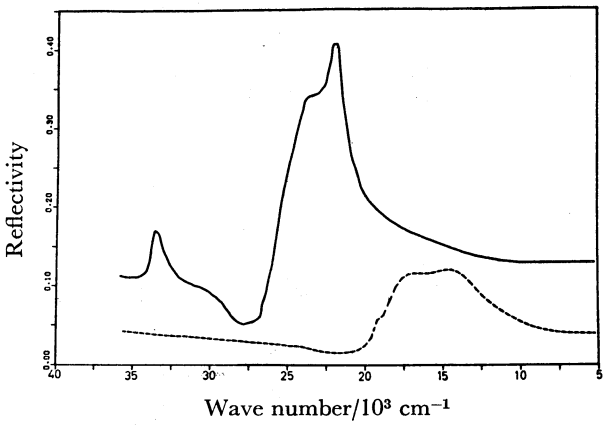

Fig. 14. The c(dashed line) and a(solid line) axes reflection spectra obtained on the (010) face of the crystal of TCNQ-carbazole complex.

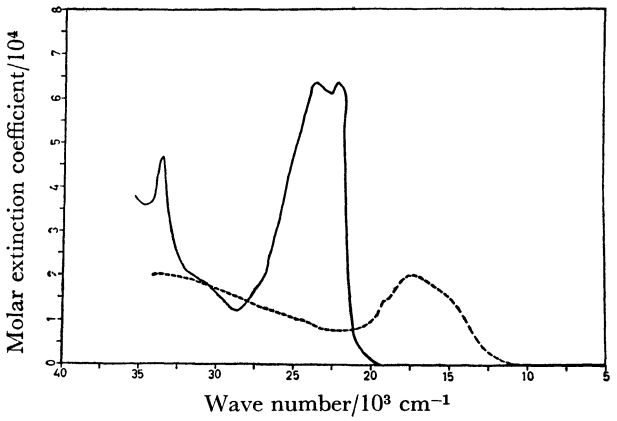

Fig. 15. The c(dashed line) and a(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ–carbazole complex.

The c-axis reflection spectrum has a band with a 12.0% reflectivity which splits into doublets at 14600 and 16600 cm^{-1}. The a-axis reflection spectrum consists of two bands. The intense band occurs at 21800 cm^{-1}, with a reflectivity of 40.6%, while the sharp band occurs at 33600 cm^{-1}, with a 17.0% reflectivity.

In the absorption spectra, the first band at 14600 cm^{-1} is active for the light parallel to the c-axis and can be assigned to the CT transition from the highest occupied carbazole orbital ($\phi_D^7(a_2)$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$). The oscillator strength of the CT band is 0.637, and the charge-transfer degree in the ground state is 12.0%. The second and third bands, at 22200 and 33600 cm^{-1}, are polarized along the a-axis, which is parallel to the long-axis of each molecule. Therefore, the 22200 cm^{-1} band can be regarded as the LE_1 band of TCNQ, and the 33600 cm^{-1} band as corresponding to the 34100 cm^{-1} band (α^* band) of the carbazole molecule in an ethanol solution.[13]

TCNQ–Hexamethylbenzene Complex. The crystals of the complex of TCNQ–hexamethylbenzene are monoclinic, and the space group is I2/m.[14] The structure consists of infinite columns of alternate molecules, and the column is parallel to the *a*-axis. The mean molecular separation is 3.55 A, and the intermolecular distance parallel to the a axis, R_{AD}, is 4.28 Å. The molecular overlap is illustrated in Fig. 16. The reflection spectra are obtained for the polarizations

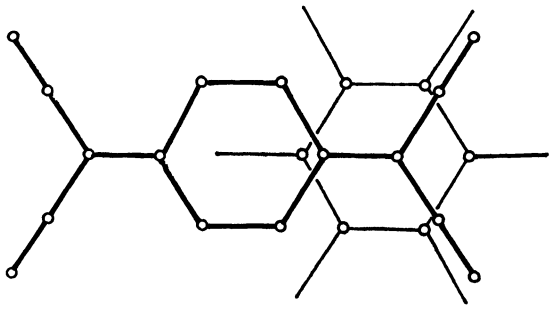

Fig. 16. The molecular overlap of the TCNQ–hexamethylbenzene complex.

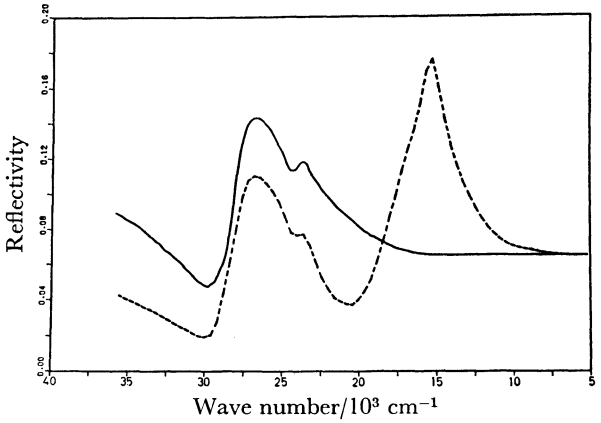

Fig. 17. The a(dashed line) and $a_\perp$(solid line) axes reflection spectra obtained on the (010) face of the crystal of TCNQ–hexamethylbenzene complex.

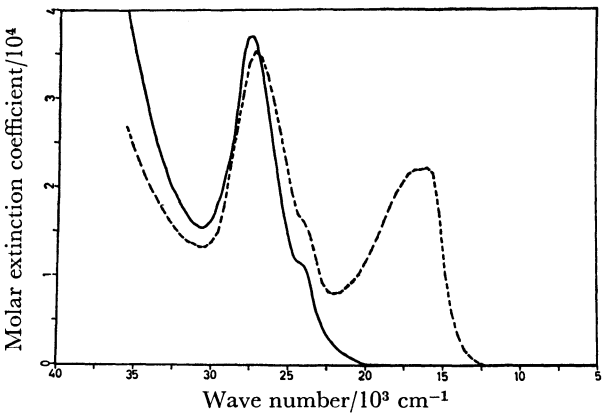

Fig. 18. The a(dashed line) and $a_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ–hexamethylbenzene complex.

parallel and perpendicular to the a-axis on the (010) face. The absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 17 and 18.

The a-axis reflection spectrum has two bands. The first band occurs at 15200 cm^{-1}, with a reflectivity of 17.6%. The second band has the 0-0 transition at 23600 cm^{-1}, and the band peak appears at 26800 cm^{-1}, with an 11.0% reflectivity. The $a_\perp$-axis reflection spectrum shows no clear structure in the first a-axis band. The band corresponding to the second a-axis band has its first peak at 23600 cm^{-1}, while the main peak is located at 26800 cm^{-1}, with a reflectivity of 14.3%.

In the absorption spectra, the first band at 16000 cm^{-1} is polarized along the a-axis and may be assigned to the CT transition from one of the highest occupied hexamethylbenzene orbitals ($\phi_D^2(e_{1g})$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$). The oscillator strength of the CT band is 0.765, and the charge-transfer degree in the ground state is 8.0%. The second band at 27400 cm^{-1} has the same magnitude of absorption intensities in the a- and $a_\perp$-axes spectra. The (010) projection shows that the long-axis of the TCNQ

molecule is inclined at an angle of 56° to the stacking axis and indicates that the long-axis transition should be observed with the comparable absorption intensities for the a and $a_\perp$ axes spectra. Therefore, the 27000 cm^{-1} band can be attributed to the LE_1 transition of the TCNQ molecule.

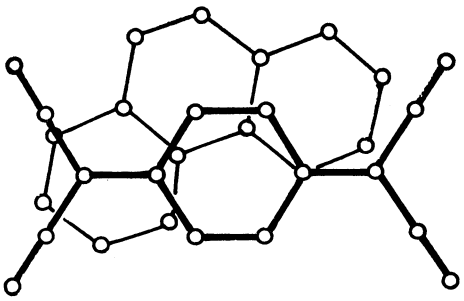

Fig. 19. The molecular overlap of the TCNQ–1,10-phenanthroline complex.

TCNQ-1,10-Phenanthroline Complex. The complex of TCNQ-1,10-phenanthroline forms a monoclinic crystal with a space group of $P2_1/n$.[15] The TCNQ and 1,10-phenanthroline molecules are packed in continuous mixed stacks usually, and the stacking axis is the c-axis. The mean interplanar donor-acceptor distance, R_{AD}, is 3.41 Å. The molecular overlap is shown in Fig. 19. The reflection spectra are observed for the polarizations parallel and perpendicular to the c-axis on the (010) face. The absorption spectra are obtained by the K-K transformation of the reflection spectra, as is shown in Figs. 20 and 21.

The c-axis reflection spectrum has a broad band at 18000 cm^{-1}, with a reflectivity of 4.6%. The $c_\perp$-axis reflection spectrum has two intense bands, at 22800 and 36800 cm^{-1}, with reflectivities of 26.7 and 19.8%.

In the absorption spectra, the first band at 20500 cm^{-1} is active for the light parallel to the c-axis and can be assigned to the CT transition from the highest occupied 1,10-phenanthroline orbital ($\phi_D^7(b_1)$) to the lowest unoccupied TCNQ orbital ($\phi_A^9(b_{1g})$). The oscillator strength of the CT band is 0.407, and the charger-transfer degree in the ground state is 5.2%.

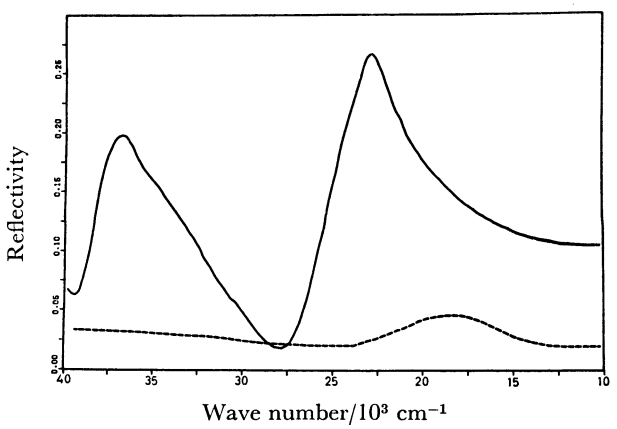

Fig. 20. The c(dashed line) and $c_\perp$(solid line) axes reflection spectra obtained on the (010) face of the crystal of TCNQ–1,10-phenanthroline complex.

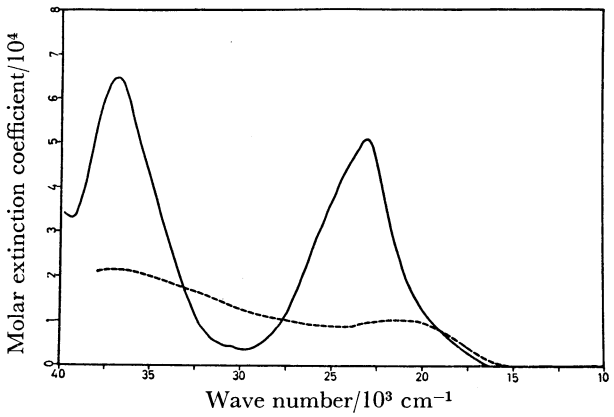

Fig. 21. The c(dashed line) and $c_\perp$(solid line) axes absorption spectra obtained by the K-K transformation of the reflection spectra of the crystal of TCNQ–1,10-phenanthroline.

The second and third bands at 23000 and 36800 cm^{-1} are polarized along the $c_\perp$-axis. The (010) projection shows that the long axes of the TCNQ and 1,10-phenanthroline molecules are nearly perpendicular to the a-axis. Therefore, the 23000 cm^{-1} band can be attributed to the LE_1 band of TCNQ, and the 36800 cm^{-1} band, to the long-axis transition of 1,10-phenanthroline.

Discussion

The energy of the CT transition, E_{CT}, is given approximately by the equation

$$E_{CT} = I_p - E_A - C - P,$$

where I_P is the ionization potential of the donor; E_A, the electron affinity of the acceptor; C, the Coulombic interaction between donor and acceptor molecules, and P, the polarization energy. That is, the observed energies (E_{CT}) of the charge-transfer transitions maintain a linear relation with the ionization potentials (I_P) of the donor molecules, as is shown in Table 1. The first CT band of the TCNQ-phenothiazine complex is located in the lowest energy region, and the CT bands of TCNQ-anthracene, pyrene, acenaphthene, and hexamethylbenzene are observed in the order of increasing energy, in the same manner as that of the ionization potential. The Coulomb energy of the first band can be estimated by the use of the Nishimoto-Mataga approximation, and the electron affinity of the TCNQ molecule was determined to be 2.80 eV by Klots, Compton, and Raaen.[16] Then, the polarzation energy, P, can be deduced as is shown in Table 1. It should be noted that the crystal of the TCNQ-phenothiazine complex has a large polarization energy (P=1.10 eV) although those of the other complexes are 0.7—0.8 eV. This extraordinary size of the crystal of the TCNQ-phenothiazine complex was also observed in the phenothiazine crystal.[17] The vertical ionization energy of a molecular crystal, I_C, is related to the ionization energy, I_P, of the corresponding gaseous molecule by the relation: $I_P = I_C + P$. Therefore, the values of $I_P - I_C$ are equal to the polarization energy, P, in the solid state; it is shown in Table 1 that the phenothiazine

crystal has a larger value of the polarization energy $P(=I_P-I_C)$ than the other compounds.

The stabilization energies in the ground state are determined by means of the equation: $\Delta E=\sum_t b_t^2 E_{CT}^t$, and are shown in Table 1. According to Table 1 and the molecular overlaps, the crystals of the complexes forming a configuration of a high symmetry like the TCNQ-anthracene and carbazole systems are more strongly stabilized by the charge-transfer force, although this seems not to be a general rule.

References

1) M. Tanaka, *Bull. Chem. Soc. Jpn.*, **50**, 2881 (1977).
2) M. Tanaka, *Bull. Chem. Soc. Jpn.*, **50**, 3194 (1977).
3) H. Kobayashi, *Acta Crystallogr., Sect. B*, **30**, 1010 (1974).
4) R. R. Pennelly and C. J. Eckhardt, *Chem. Phys.*, **12**, 89 (1976).
5) R. M. Williams and S. C. Wallwork, *Acta Crystallogr., Sect. B*, **24**, 168 (1968).
6) C. J. Eckhardt and R. R. Pennelly, *J. Am. Chem. Soc.*, **98**, 2034 (1976).
7) L. B. Clark and M. R. Philpott, *J. Chem. Phys.*, **53**, 3790 (1970).
8) C. K. Prout, I. J. Tickle and J. D. Wright, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 528.
9) J. Tanaka, *Bull. Chem. Soc. Jpn.*, **38**, 86 (1965).
10) I. J. Tickle and C. K. Prout, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 727.
11) M. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 2315 (1976).
12) H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **46**, 2675 (1973).
13) M. Tanaka, *Bull. Chem. Soc. Jpn.*, **49**, 3382 (1976).
14) R. H. Colton and D. E. Henn, *J. Chem. Soc., B*, **1970**, 1532.
15) I. Goldberg and U. Shmueli, *Cryst. Struct. Commun.*, **2**, 175 (1973).
16) C. E. Klots, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.*, **60**, 1177 (1974).
17) F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley and Sons, New York (1967), pp. 351, 667.