0.85 (Table III). It should be recalled that **R** for **2a** (Figure 5) at the limit of large barrier is 0.50. While it is tempting to utilize the Stone–Maki model to estimate $V_0 \sim 4$ kcal mole^{-1} it is also clear from the absence of C_{2v} symmetry (*vide infra*) that the approximation of a simple twofold barrier is *not* applicable; thus a barrier cannot be evaluated quantitatively. The schematic representation of conformation in Figure 6a is consistent with both alkyl proton and nitrogen coupling constants.

By comparison with the range of **R** values for *p*-isopropylnitrobenzene anion, 0.44–0.47, the value of 0.36 for *o*-isopropylnitrobenzene anion is also considerably reduced. This value of **R** corresponds to $V_0 =$ 1.3 kcal mole^{-1} for conformation **1a** (Figure 5); since the barrier is not strictly twofold, this value can only be regarded as indicative. The schematic representation in Figure 6b combines data for both nitrogen and proton coupling constants. A substantially larger nitrogen coupling constant would be expected if the two isopropyl methyl groups were *cis* to the nitro group (Figure 6c) rather than *trans* (Figure 6b). Therefore, we can infer that the spatial requirements of the two methyl groups cause the preferred orientation to be that shown in Figure 6b.

The question of the conformation of the neutral parent molecules, the 2-alkylnitrobenzenes, has been examined on the basis of spectrophotometric data.[59] The twist angles for the nitro group inferred for the various substituents were 2-methyl, 34°; 2-ethyl, 40°; 2-isopropyl, 47°; and 2-*t*-butyl, 65°. The abrupt increase in the twist angle for the *t*-butyl derivative was ascribed to the fact that all the other groups have at least one β-hydrogen atom which permits a favorable orientation such as Figure 6b.

Electrochemistry. Esr data provide an understanding of the structure of the anion radical. By contrast standard electrode potentials as approximated by half-wave potentials are dependent on the free-energy difference between the neutral molecule and the anion. The change in half-wave potential attributable to steric effects, ΔE_s,[5] for the *o*-alkylnitrobenzene as computed from data in Table I are 0.06, 0.05, 0.09, and 0.16 v,[60] for methyl, ethyl, isopropyl, and *t*-butyl, respectively. The abrupt effect of the *t*-butyl groups on ΔE_s parallels the change of a_N with alkyl substitution.

Acknowledgment. The authors acknowledge support from the National Science Foundation through Grants GP-1985 and GP-4906 as well as through GP-1687 for partial support for purchase of the esr spectrometer. We are indebted to Professor B. M. Wepster for a gift of 2-isopropylnitrobenzene.

[59] B. M. Wepster, *Progr. Stereochem.*, **2**, 110 (1950).

[60] Since $E_{1/2}$ for 4-*t*-butylnitrobenzene is not available, a value of 1.19 v *vs.* sce was assumed in the calculation of ΔE_s.

Absorption and Emission Spectra of 1,2,4,5-Tetracyanobenzene–Naphthalene Complex Crystal

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Abstract: The electronic absorption and emission spectra of the charge-transfer complex of 1,2,4,5-tetracyanobenzene with naphthalene were studied by measuring them under various conditions, and by carrying out a theoretical study on the basis of configuration interaction among the ground, locally excited, and charge-transfer configurations. By combining the theoretical results with the polarized absorption measurements of the single crystal, it is concluded that the longest wavelength band at 24,600 cm^{-1} may be ascribed to the first charge-transfer transition, and that the second charge-transfer band appears at 31,500 cm^{-1} overlapping with local excitation bands. The fluorescence spectrum of the crystal at liquid N_2 temperature, which commences at 23,200 cm^{-1} and shows vibrational structure, nicely satisfies the well-known mirror image relation to the first charge-transfer band. On the other hand, the fluorescence spectrum of the crystal at room temperature is structureless and is shifted to lower frequencies compared with that at liquid N_2 temperature. The phosphorescence spectrum of the complex observed at liquid He temperature shows well-resolved vibrational structure which is satisfactorily coincident with that of the phosphorescence spectrum of naphthalene itself. This means that the phosphorescent state of the complex may be regarded as the locally (within naphthalene) excited triplet state.

The electronic spectra of charge-transfer (abbreviated hereafter to CT) complexes in crystalline state are interesting research subjects in connection with the CT theory developed by Mulliken.[1] The experimental evidence for the existence of the CT absorption can be obtained from the directions of the transition moments of the bands determined by polarized absorption measurements of single crystals, and the study of absorption and emission spectra of CT complexes may give valuable information about the interaction between the CT and locally excited structures and about electron- and energy-transfer phenomena in CT complex crystals. So far, however, the measurements of polarized absorption spectra have been carried out with rather few CT complex crystals, although many studies have been done with electronic spectra of solutions.[2,3] The most

[1] R. S. Mulliken, *J. Chim. Phys.*, **61**, 20 (1963).

[2] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

[3] L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

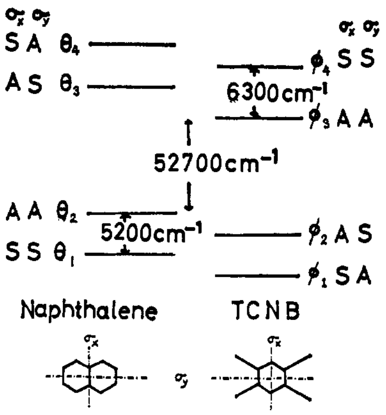

Figure 1. The orbital symmetries of the naphthalene and TCNB molecules and the differences of the orbital energies. $\epsilon(\theta_2) - \epsilon(\theta_1)$ and $\epsilon(\phi_4) - \epsilon(\phi)_3$ are estimated by the multi-CT bands. $\epsilon(\phi_3) - \epsilon(\theta_2)$ is the difference between the ionization potential (I_p) of donor and the electron affinity (A_f) of acceptor. According to the photoionization experiment (F. I. Vilisov, *Soviet Phys. Usp.* (Engl. Transl.), **6**, 888 (1964); *Usp. Fiz. Nauk*, **81**, 669 (1963)), I_p is 8.13 ev. A_f was estimated to be 1.60 ev by the aid of the CT band positions of some complexes in the previous paper.[8]

extensive studies on the polarized absorption and fluorescence spectra of single crystals have been done for the trinitrobenzene–anthracene complex.[4–7] Hochstrasser and his co-workers observed the vibrational structure in the CT band at room and liquid N_2 temperatures,[4] and they inferred the existence of localized excitons from experimental results showing that the absorption and fluorescence polarization ratios at 300°K are very different from each other.[5] Further, they reported that the CT transition intensity in the crystal is about twice that in solution.[6]

In a previous paper[8] we reported on the absorption spectra of the 1,2,4,5-tetracyanobenzene (TCNB)–mesitylene complex crystal and showed that the absorption band of the acceptor (TCNB) is changed in the complex as a result of the mixing of the CT structure with the TCNB locally excited electronic structure.

The present paper is concerned with the absorption, fluorescence, and phosphorescence spectra of the TCNB–naphthalene complex crystal. We measured the spectra at various temperatures and considered them theoretically by the semiempirical MO method, using the crystal structure of the complex recently determined by Kumakura, Iwasaki, and Saito.[9]

Experimental Section

TCNB was prepared by Ishitani and Maruyama of our laboratory by the method described in the previous paper.[8] Naphthalene was purified by repeated recrystallizations in ethanol. The TCNB–naphthalene complex crystal was prepared by mixing the acceptor and the donor in methylene chloride and by evaporating the solvent at room temperature.

The absorption spectra in solution and in thin film were measured with a Cary recording spectrophotometer, Model 14 M. A spectrophotometer attached with a microscope and a Roschen-type polarizer[10] was used for the polarized ultraviolet absorption measurement of single crystals. The emission spectra at room and liquid N_2 temperatures were measured with a JASCO Model CT-50 grating monochrometer with a RCA 1P28 or EMI 9529 A photomultiplier tube as detector, and those at liquid H_2 and liquid He temperatures with a Fuess prism monochrometer, Kodak 103a F plates being used.

Theoretical Section

In the previous paper[8] we calculated the electronic structures of the TCNB complexes with methyl-substituted benzenes. Consequently we could predict some possible stable geometrical structures of the complexes.[11] Furthermore, it was demonstrated that the mixing of the CT configuration with the acceptor locally excited configurations plays an important role in the excited states of some CT complexes. A similar theoretical consideration has been made for the TCNB–naphthalene complex on the basis of the structure determined by the X-ray crystal analysis technique.

For the sake of simplicity, only the highest two occupied (ϕ_1, ϕ_2 and θ_1, θ_2) and lowest two vacant molecular orbitals (ϕ_3, ϕ_4 and θ_3, θ_4) of TCNB and naphthalene[13] were considered. The symmetry and energy of each orbital are shown in Figure 1. The wave function of the ground configuration is given by the Slater-type determinant

$$\Phi_G = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\theta_1\bar{\theta}_1\theta_2\bar{\theta}_2| \tag{1}$$

The lowest CT configurations are

$$\begin{aligned} \Phi_{CT_1} &= \Phi(\theta_2{}^{-1}\phi_3) \\ \Phi_{CT_2} &= \Phi(\theta_1{}^{-1}\phi_3) \\ \Phi_{CT_3} &= \Phi(\theta_2{}^{-1}\phi_4) \\ \Phi_{CT_4} &= \Phi(\theta_1{}^{-1}\phi_4) \end{aligned} \tag{2}$$

The lowest two locally excited configurations of TCNB and of naphthalene are approximately written as[15]
for TCNB

$$\begin{aligned} \Phi_{L1} &= 0.7878\Phi(\phi_1{}^{-1}\phi_3) + 0.6159\Phi(\phi_2{}^{-1}\phi_4) \\ \Phi_{L2} &= -0.5032\Phi(\phi_1{}^{-1}\phi_4) + 0.8642\Phi(\phi_2{}^{-1}\phi_3) \end{aligned} \tag{3}$$

for naphthalene

$$\begin{aligned} \Phi_{L3} &= \frac{1}{\sqrt{2}}\{\Phi(\theta_1{}^{-1}\theta_3) + \Phi(\theta_2{}^{-1}\theta_4)\} \\ \Phi_{L4} &= \Phi(\theta_2{}^{-1}\theta_3) \end{aligned} \tag{4}$$

where

$$\Phi(\theta_i{}^{-1}\phi_j) = \frac{1}{\sqrt{2}}\{|\ldots\theta_i\bar{\phi}_j\ldots| + |\ldots\phi_j\bar{\theta}_i\ldots|\}$$

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(4) S. K. Lower, R. M. Hochstrasser, and C. Reid, *Mol. Phys.*, **4**, 161 (1961).

(5) R. M. Hochstrasser, S. K. Lower, and C. Reid, *J. Chem. Phys.*, **41**, 1073 (1964).

(6) R. M. Hochstrasser, S. K. Lower, and C. Reid, *J. Mol. Spectry.*, **15**, 257 (1965).

(7) J. Tanaka and K. Yoshihara, *Bull. Chem. Soc. Japan*, **38**, 739 (1965).

(8) S. Iwata, J. Tanaka, and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

(9) S. Kumakura, F. F. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, in press.

(10) J. Tanaka, *ibid.*, **36**, 833 (1963).

(11) Recently Niimura, Ohhashi, and Saito determined the structure of the hexamethylbenzene (HMB)–TCNB complex by the aid of the X-ray crystal analysis technique.[12] The results are in good agreement with our expectation on the stable configuration. The center of HMB molecule is located above one of the C–C bonds of the TCNB benzene ring.

(12) N. Niimura, Y. Ohhashi, and Y. Saito, General Symposium on Molecular Structure and Spectroscopy, Osaka, Japan, Oct 1966.

(13) The self-consistent field molecular orbitals of TCNB and naphthalene are determined using the Pariser–Parr–Pople approximations. The parameters used for TCNB were described in the previous paper,[8] and Pariser's parameters[14] were used for naphthalene.

(14) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(15) The wave functions of the locally excited configurations were determined by the configuration interaction including the one-electron excited configurations which are composed of the four orbitals considered.

The configuration interaction among the above nine electron configurations was considered. The energies of the excited configurations Φ_{L1}, Φ_{L2}, Φ_{L3}, and Φ_{L4} are taken to be equal to the corresponding transition energies observed with TCNB and naphthalene, the energy of the ground configuration Φ_G being taken to be the standard: $E_G = 0$, $E_{L1} = 3.93$, $E_{L2} = 4.66$, $E_{L3} = 4.06$, $E_{L4} = 4.43$. The energies of the CT configurations, the CT_1 configuration being taken as an example, can be estimated as

$$E_{CT_1} \cong +\epsilon(\phi_3) - \epsilon(\theta_2) - \int \phi_3(1)\phi_3(1)\frac{e^2}{r_{12}}\theta_2(2)\theta_2(2) \times \mathrm{d}\tau_1\mathrm{d}\tau_2 = I(\theta_2) - A(\phi_3) - C_{23} \quad (5)$$

where $\epsilon(\phi_3)$ and $\epsilon(\theta_2)$ are the orbital energies, and $I(\theta_2)$ and $A(\phi_3)$ are the ionization potential of the donor and the electron affinity of the acceptor, respectively (see Figure 1). C_{23} is the Coulomb repulsion energy between two electrons belonging to ϕ_3 and θ_2 orbitals. In fact, it is evaluated with the aid of the point-charge approximation. In the above expressions for the configuration energies the following two approximations are adopted. (1) The electrostatic interaction energies between the two component molecules are equal in the ground and locally excited configurations, because both the donor and acceptor molecules have no dipole moment and so the electrostatic interaction is thought to be very small. (2) The overlap integrals between the donor and acceptor orbitals are neglected.

Using the SCF MO of the isolated constituent molecules, we can write the off-diagonal elements of the total electron Hamiltonian which represent the interaction of the ground configuration with the excited configurations as[16]

$$\langle\Phi_G|H|\Phi(\theta_i^{-1}\phi_{j'})\rangle - \langle\Phi_G|\Phi(\theta_i^{-1}\phi_{j'})\rangle E_0 = \sqrt{2}\Big[\Big(i\,\Big|\,-\frac{1}{2}\Delta + V(\mathrm{A}) + V(\mathrm{D}_i^{+})\,\Big|\,j'\Big) - S_{ij'}\{\epsilon_i + J_{ii}\} - \sum_{k'}S_{ik'}(k'|V(\mathrm{D}_i^{+})|j') - \sum_{k}S_{kj'}(k|V(\mathrm{A})|i)\Big] \quad (6)$$

where operators $V(\mathrm{A})$, $V(\mathrm{D})$, and $V(\mathrm{D}_i^{+})$ are defined as[17]

$$(\varphi_j|V(\mathrm{D})|\varphi_i) = -\sum_d\int\varphi_j^*(1)\frac{Z_d}{r_{d1}}\varphi_i(1)\mathrm{d}\tau_1 + \sum_k\{2(\varphi_j\varphi_i|kk) - (\varphi_jk|k\varphi_i)\}$$

$$(\varphi_j|V(\mathrm{D}_i^{+})|\varphi_i) = (\varphi_j|V(\mathrm{D})|\varphi_i) - (\varphi_j\varphi_i|ii) + (\varphi_ji|i\varphi_i)$$

and

$$(\varphi_j\varphi_i|\varphi_k\varphi_l) = \int\varphi_j^*(1)\varphi_k^*(2)\frac{1}{r_{12}}\varphi_i(1)\varphi_l(2)\,\mathrm{d}\tau_1\mathrm{d}\tau_2$$

In eq 6, the terms higher than second order with regard to S are neglected. The first and second terms of this equation contribute mainly to the value of the integral. The third and fourth terms are thought to be small compared with the first and second terms and may be neglected. Nonempirical evaluations of the terms in eq 6 are so difficult that we evaluate them semiempirically

$$\langle\Phi_G|H|\Phi(\theta_i^{-1}\phi_{j'})\rangle - \langle\Phi_G|\Phi(\phi_i^{-1}\phi_{j'})\rangle E_0 = \sqrt{2}(-KS_{ij'}) \quad (6')$$

The other important type of the off-diagonal elements are those between the CT and locally excited configurations (eq 7). The semiempirical parameters K

$$\langle\Phi(\theta_i^{-1}\phi_{j'})|H|_j\Phi(\phi_{i'}^{-1}\phi_{j'})\rangle - \langle\Phi(\theta_i^{-1}\phi_{j'})|\Phi(\phi_{i'}^{-1}\phi_{j'})\rangle E_0 = -\Big(i'\Big|-\frac{1}{2}\Delta + V(\mathrm{D}_i^{+}) + V(\mathrm{A})\Big|i\Big) - (j'j'|i'i) + 2(j'i|i'j') - S_{ii'}(+\epsilon_{j'} - \epsilon_i - \epsilon_{i'} - J_{ii} - J_{i'i'}) + S_{ij'}(i'|V(\mathrm{D}_i^{+})|j') + \Sigma S_{ik'}[(i'|V(\mathrm{D}_i^{+})|k') + (j'j'|i'k') - (j'k'|i'j')] + \Sigma S_{i'k}[(i|V(\mathrm{A}_{i'}^{+})|k) + (j'j'|ik) - (j'k|ij')] \simeq -K'S_{ii'} \quad (7)$$

and K' in eq 6′ and 7 are not exactly the same, but we set both $K \simeq 10$.[8] For calculating the overlap integrals, Roothaan's expanded Hartree–Fock atomic orbital functions[18] were used.

The interaction between the locally excited configurations of different molecules can be expressed as

$$\langle\Phi(\theta_i^{-1}\theta_j)|H|\Phi(\phi_{i'}^{-1}\phi_{j'})\rangle - \langle\Phi(\theta_i^{-1}\theta_j)|\Phi(\phi_{i'}^{-1}\phi_{j'})\rangle E_0 = 2(ji|j'i') - (jj'|i'i) - S_{jj'}\Big(i\Big|-\frac{1}{2}\Delta + V(\mathrm{A}) + V(\mathrm{D})\Big|i'\Big) - S_{ii'}\Big(j\Big|-\frac{1}{2}\Delta + V(\mathrm{A}) + V(\mathrm{D})\Big|j'\Big) \simeq 2(ji|j'i') \quad (8)$$

The off-diagonal term between two CT configurations can be expressed by the equation similar to the above. This is the interaction energy between two transition charge densities. For the interaction between the two CT configurations, the interaction energy was calculated by the point-charge approximation. On the other hand, the interaction energy between the two locally excited configurations was estimated by using the experimental transition dipoles because the wave functions of the locally excited configurations in which only the four orbitals are included are not good enough to give agreement between the calculated transition moments and the observed values. Also, the transition charge density of the lowest excited state Φ_{L3} of naphthalene is zero within LCAO–MO approximation.

Results and Discussion

The Structure of the Naphthalene–TCNB Complex. In a structure where the center of a donor molecule is located just above that of the acceptor and the long axis of one molecule is parallel to that of the other, the lowest CT configuration, $\Phi(\theta_2^{-1}\phi_3)$, can mix with the ground configuration because the orbitals θ_2 and ϕ_3 have same symmetry. The stabilization energy ΔE due to CT interaction was evaluated for this model and for two series of the geometrical models.

First, we allow one molecule to rotate around the axis perpendicular to molecular plane fixing the centers of the molecules. All four CT configurations under

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(16) The matrix elements in the variation method including the overlap integrals are $\mathcal{H} - S\epsilon$. As we take the energy E_0 of the ground configuration as standard,

$$\mathcal{H} - S\epsilon = (\mathcal{H} - SE_0) - SE$$

so $H_{12} - S_{12}E_0$ is the off-diagonal element considered.

(17) J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 5037 (1959).

(18) E. Clementi, "Tables of Atomic Functions," a supplement to the paper which appears in *IBM J. Res. Develop.*, **9**, 2 (1965).

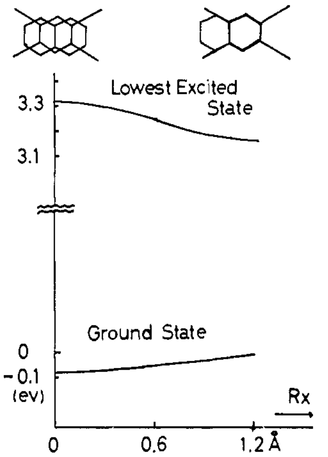

Figure 2. The potential curves calculated for the ground and lowest CT excited states. When $R_x = 0$, the center of TCNB molecule is located just above that of the naphthalene molecule. When $R_x = 1.2$ A, there is the benzene ring of TCNB just over one benzene ring of naphthalene.

consideration stabilize the ground state, and the calculated stabilization energy is little dependent on the rotation angle θ; for example, when $\theta = 0°$, $\Delta E = -0.09$ ev, and, when $\theta = 90°$, $\Delta E = -0.08$ ev. On the other hand, in these structures the lowest four locally excited configurations of the donor and acceptor and the four CT ones do not interact at all because of the symmetry of the orbitals.

Next, we try to shift one molecule along the x direction which is parallel to the long axis of molecules. The calculated potential curves for the ground and lowest excited states are shown in Figure 2. This time the stabilization energy changes from -0.09 to -0.01 ev with increasing R_x from 0 to 1.20 A, where R_x is the x coordinate of the center of one molecule when the origin is taken to be the center of the other. When $R_x \neq 0$, the interaction between the lowest CT configuration and the lowest excited configuration within the donor and acceptor occurs, so that the lowest CT excited state is lowered from 3.32 to 3.17 ev with changing R_x from 0 to 1.20 A. A similar result was obtained when one molecule is shifted along the short axis of the other molecule.

Thus the theoretical results seem to show that the stable structure in the ground state may be the structure in which the center of one molecule is located just above that of the other.

The crystal structure of TCNB–naphthalene complex has been determined by Kumakura, Iwasaki, and Saito.[9,19] According to their results, the donor and acceptor molecules are stacked alternately in columns parallel to the c axis, and their planes are nearly perpendicular to this axis. Figures 3a and b show projections of TCNB and naphthalene molecules onto the plane perpendicular to the c axis and the {110} face of the complex crystal, respectively. According to Figure 3a the center of one molecule is just above that of the other molecule, and the long axis of naphthalene molecules in the complex is at an angle of θ (θ is about 20°) with respect to the a' axis which is parallel to the long axis of TCNB molecule.[20]

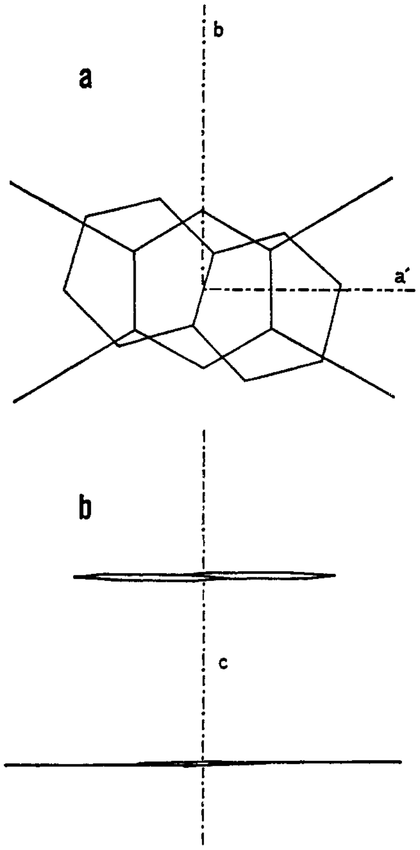

Figure 3. (a) Projection onto a plane perpendicular to the c axis. (b) Projection onto the {110} face, in which the absorption measurements were made.

Thus the structure in crystal is coincident with our theoretical expectation. From this it may be inferred that the stacking of the molecules in this crystal may be mainly controlled by the CT force.[21] On the basis of the structure determined by the X-ray crystal analysis technique, the energy levels and wave functions of the ground and excited states of the complex have been calculated by the method described in the Theoretical Section. The results are given in Table I.

The Crystal Absorption Spectra. The visible and near-ultraviolet absorption spectra of the single crystal measured at room temperature are shown in Figure 4a. They have two peaks polarized parallel to the c axis and one peak polarized perpendicular to it. By comparing them with the solution spectra of TCNB, naphthalene, and the TCNB–naphthalene complex shown in Figure 4b, it is concluded that the first band at 25,000 cm^{-1} in crystal and in solution can be regarded as the CT band. The absorption intensity

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(19) The crystal is monoclinic and the space group is C2/m, with the two complexes in a unit cell. The complex crystallizes as needles, with the long axis parallel to c. The centers of TCNB molecules occupy (0, 0, 0) and ($^1/_2$, $^1/_2$, 0) positions in a unit cell, while those of naphthalene molecules are placed in (0, 0, $^1/_2$) and ($^1/_2$, $^1/_2$, $^1/_2$) positions.

(20) The angle may be either $+\theta$ or $-\theta$. This disorder does not affect the discussion on the polarization of the CT bands, but the polarization of the intramolecular local excitations of naphthalene in the {110} face should be carefully discussed, because both short and long axes of naphthalene molecules are projected onto the {110} face at different angles between molecules with an angle of $+\theta$ and $-\theta$.

(21) In some CT complex crystal, the steric factor, a methyl group, plays an important role in the way of stacking. The TCNB–TMPD complex is a case in point.[22] On the other hand, in HMB–TCNB complexes, molecules are so nicely stacked that the CT force is strong (see ref 11).

(22) Y. Ohhashi, H. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, in press.

Table I. Wave Functions of a 1 : 1 TCNB–Naphthalene Complex[a]

(a) Wave Functions of Ground and Lowest Four CT States

Energy, W_i, ev	$W_i - W_0$, cm^{-1}	Coefficients Φ_G	Φ_{CT_1}	Φ_{CT_2}	Φ_{CT_3}	Φ_{CT_4}
W_0 −0.09	0	0.9886	0.1173	0.0421	−0.0604	0.0595
W_1 3.32	27,500	−0.1109	0.9908	−0.0504	0.0566	−0.0174
W_2 3.89	32,100	−0.0334	0.0340	0.9756	0.2138	−0.0149
W_4 4.00	33,000	0.0736	−0.0575	−0.2091	0.9731	0.0265
W_7 4.62	38,000	−0.0624	0.0113	−0.0124	−0.0244	0.9976

(b) Wave Functions of TCNB and Naphthalene Locally Excited States

W_i, ev	$W_i - W_0$, cm^{-1}	Coefficients Φ_{L1}	Φ_{L2}	Φ_{L3}	Φ_{L4}
W_3 3.93	32,400	0.9974	−0.0075	−0.060	+0.0381
W_5 4.06	33,500	+0.0598	−0.0177	0.9980	0.0104
W_6 4.35	35,800	−0.0384	−0.4523	−0.0150	0.8909
W_8 4.74	38,200	−0.0099	0.8917	0.0117	0.4525

[a] The theoretical consideration has been made with the complex with geometrical orientation in crystal. The ground and lowest four CT configurations are little mixed with the TCNB and naphthalene locally excited configurations because of the molecular orbital symmetry.

ratio ($A_{\parallel}/A_{\perp}$) for light polarized parallel and perpendicular to the *c* axis is far larger than 25 : 1.

According to the X-ray crystal analysis data, TCNB and naphthalene molecules are stacked alternately in columns parallel to the *c* axis, and the centers of the molecules are on the *c* axis. Therefore we can safely say that the direction of the transition moment of the first band at 25,000 cm^{-1} is nearly parallel to the line connecting the centers of the two component molecules. This fact supports the interpretation of this band as the first CT band.

The second band in the ~33,000–29,000-cm^{-1} is also polarized parallel to the *c* axis. This means that this band can be assigned to a CT transition as well. From the theoretical point of view, the appearance of two CT bands in the ~25,000–35,000-cm^{-1} region is quite reasonable.

From the calculated energy levels given in Table I, the transition energies $W_i - W_0$ can be evaluated and these are given in the same table. The results show that five absorption bands corresponding to the $W_0 \rightarrow W_i$ (i = 1–5) transitions appear in the ~25,000–35,000-cm^{-1} region. From the wave functions given in Table I, it is revealed that the $W_0 \rightarrow W_1$, $W_0 \rightarrow W_2$, and $W_0 \rightarrow W_4$ transitions are of CT character, and the $W_0 \rightarrow W_3$ and $W_0 \rightarrow W_5$ transitions of local excitation. The first CT band at 25,000 cm^{-1} clearly corresponds to the $W_0 \rightarrow W_1$ transition and is due to the transition from the highest occupied orbital (θ_2) of naphthalene to the lowest vacant orbital (ϕ_3) of TCNB. There are two possibilities for the interpretation of the second CT band. One of them is the transition from the second highest occupied (θ_1) orbital of naphthalene to the lowest vacant orbital (ϕ_3) of TCNB, and the other is the one from the highest occupied orbital (θ_2) of naphthalene to the second lowest vacant orbital (ϕ_4) to TCNB (see Figure 1). The separation of $\Delta\nu_{CT}$ between the first and second CT bands may be expected to be 5200 cm^{-1} for the former case from the corresponding values for the naphthalene complexes containing tetracyanoethylene (TCNE) and chloranil as electron acceptor.[2] On the other hand, the $\Delta\nu_{CT}$ value for the latter case was evaluated by us[8] to be 6300 cm^{-1} from the analysis of the absorption spectra of various TCNB complexes with substituted benzenes. The tentative $\Delta\nu_{CT}$ values for the two cases are rather close to each other, and either of them can explain the observed position of the second CT band. Therefore, the observed second CT band may be due to both the above-mentioned transitions. The observed absorption intensity ratio of the first CT band to the second is about 1 : 0.88, while the calculated transition probability ratio of the first transition to the second plus the third one is 1 : 0.68.

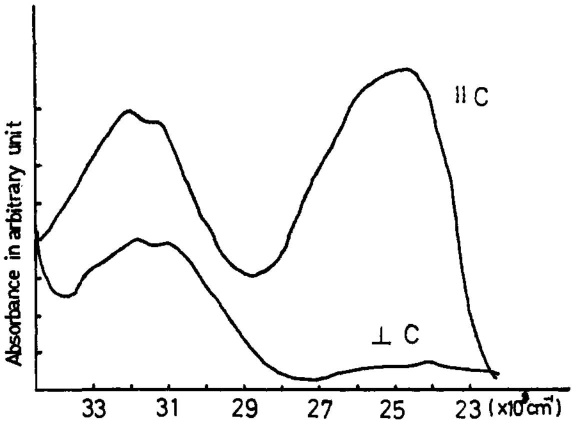

Figure 4a. The absorption spectra of the single crystal of the complex in the {110} face at room temperature. The ordinate is the absorbance in arbitrary units.

There appears in the 33,000–29,000-cm^{-1} region another band which is polarized almost perpendicular to the *c* axis. From the direction of the transition moment, this band may be regarded as due to the intramolecular local excitations of the respective component molecules. In fact, the TCNB and naphthalene molecules show absorption bands with vibrational structures in this region as is shown in Figure 4b.[23] As the absorption intensity of TCNB local excitation is larger by about 10 times than that of naphthalene, the observed band at 31,000 cm^{-1} perpendicular to the *c* axis is assigned to the TCNB local excitation. In the crystal,

(23) The first absorption band of the TCNB crystal which was observed in the previous paper[8] is little perturbed by crystal field, and its position and vibrational structure are very similar to those of the solution spectrum. On the other hand, the absorption spectrum of the naphthalene crystal is known to be different from the spectrum in solution. In our case we should compare the absorption of naphthalene in the complex with that in solution or in solid mixed solution.

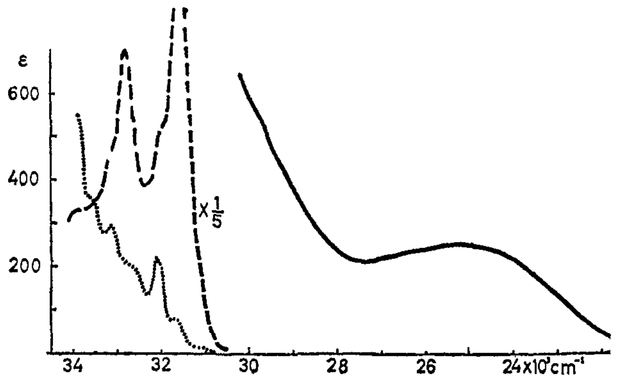

Figure 4b. The absorption spectra of naphthalene (. . . .) and TCNB (- - - -) in CH_2Cl_2. The absorption spectrum of the CH_2Cl_2 solution containing naphthalene (0.065 *M*) and TCNB (0.0009 *M*) (———), the absorption intensity of which is shown in arbitrary units.

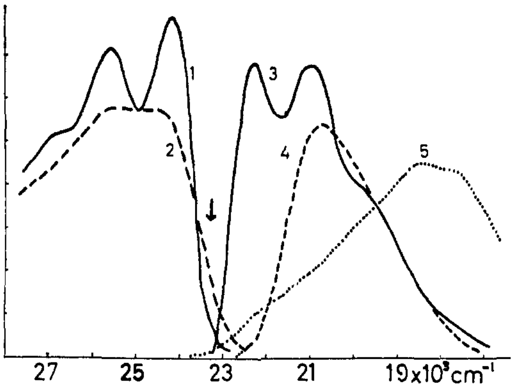

Figure 6. The absorption and fluorescence spectra of the complex: (1 and 2) the absorption spectra of the thin film on a quartz plate at 113 and 298°K, respectively (the ordinate is the absorbance in arbitrary unit); (3 and 4) the fluorescence spectra of the micro-crystal at 77 and 298°K, respectively (the ordinate is the emission intensity); (5) the fluorescence spectra of the thin film at 298°K (see ref 28).

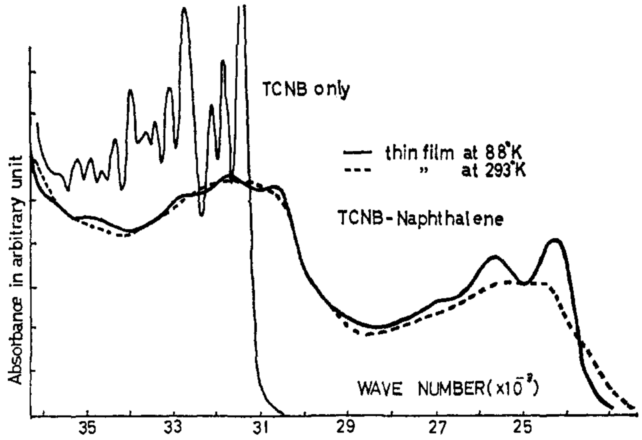

Figure 5. The absorption spectra of the thin film of the complex and TCNB only on a quartz plate. The ordinate is the absorbance in arbitrary unit: ———, complex at 88°K; - - - -, complex at 298°K; ———, TCNB only at 88°K.

the vibrational structure is blurred and the spectrum becomes broad as a whole. The reason for this is discussed in a later part of the present paper by taking into consideration the observed absorption spectra at low temperature.

In connection with the interpretation of the absorption spectrum of the CT complex, it seems to be interesting to measure it at low temperature. It is difficult, however, to do this with the single crystal principally because of technical difficulties. We prepared the thin film of the TCNB complex with naphthalene on a quartz plate and measured its absorption spectrum at 88°K.[24] The results are shown in Figure 5.[25] At 88°K vibrational structures in the first CT band appear clearly at 24,300, 25,600, and 26,800 cm^{-1}, while the tail extending to the longer wavelength region of the first band at room temperature disappears. This seems to mean that the transition bands from thermally excited vibrational states of the ground state, the so-called hot bands, provide the explanation of the tail in the longer wavelength side of the first CT band.

The absorption bands of the complex in the shorter wavelength region, which are broad at room temperature, become a little sharp at 88°K and exhibit three indistinct peaks at 30,600, 31,800, and 32,700 cm^{-1} (see Figure 5). We also measured the absorption spectrum of TCNB itself under the same conditions. The result is shown in Figure 5 for the purpose of comparison. As is clearly seen in Figure 5, the vibrational structure of the latter is much more distinct than that of the former. From the above-mentioned facts, it might be inferred that the absorption spectrum of the complex at room temperature becomes broad for the following two reasons: first, because of the presence of hot bands due to the shallowness of the ground-state potential energy curve; second, because of the interaction of the locally excited configuration of TCNB with some high-energy configurations which were not considered in our theoretical study.[26]

Fluorescence Spectra of Complex Crystal. The fluorescence spectra of the complex crystal at room and liquid N_2 temperatures are shown in Figure 6, together with the absorption spectra. The fluorescence spectra at liquid H_2 and liquid He temperatures are the same as at liquid N_2 temperature. A good mirror image relation between the fluorescence spectrum and the CT absorption spectrum is found at liquid N_2 temperature, so that the fluorescent state is concluded to be the lowest CT state. The overlap between the fluorescence and absorption spectra in the 23,200-cm^{-1} region is very small. This suggests that the geometric structure of the fluorescent state may be different from that of the ground state of the complex.

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(24) We are indebted to Mr. T. Sakata for this method of absorption measurement at low temperature. He and the present authors have checked the reliability of this method with various samples. This method is known to give the results similar to those obtained by refraction method or by microscopic method with single crystals.

(25) The absorption intensity ratio of the 32,000-cm^{-1} bands to the 25,000-cm^{-1} band is about 2.1:1 in the spectra measured with the thin film of the CT complex, while the corresponding value for the single crystal is about 1.3:1. These results do not conflict with each other, because in the single crystal the CT band at 25,000 cm^{-1} was observed in the direction of *c* axis under the most optimal conditions, but the transition moments of the local excitation bands at 32,000 cm^{-1} with the polarization in the long axis of the component molecules are projected on the perpendicular direction to the *c* axis in the {110} plane with an angle φ ($\varphi = \tan^{-1} b/a'$) $\simeq 55° 40'$.

(26) Because of the relative orientation of donor and acceptor molecules in crystal and the symmetry of the excited states, both local excitations considered are little mixed with the lowest four CT configurations, and the interactions between the donor and acceptor local excitations may be small in view of the low transition intensities.

In the case of the naphthalene–TCNB complex crystal, the Franck–Condon principle leads to the conclusion that the absorption intensity of the CT transition is small when both the ground state and the CT excited state are coupled with neither intramolecular nor intermolecular vibrations. Therefore the excited state corresponding to the longest wavelength absorption peak at 24,300 cm^{-1} seems to be coupled with some intermolecular vibrations. The similar consideration may also be applied to the fluorescence.

At room temperature the mirror image relation between the absorption spectrum and the fluorescence spectrum of the microcrystal is not satisfied. One of the reasons for this may be the reabsorption corresponding to the long tail which was interpreted as the hot band. Another reason is that the fluorescence at room temperature may be a type of "excimer emission" as in the perylene β crystal.[27] The formation of the "excited complex" might be possible at room temperature. The excited molecule is displaced over a barrier to the more stable structure, which may be stabilized by the interactions between the CT and locally excited electronic configurations.[28,29]

Phosphorescence Spectra of the CT Complex in a Crystal. A phosphorescence was observed with the crystal of the naphthalene–TCNB complex at low temperature. Figure 7 shows the phosphorescence spectra at liquid N_2 and liquid He temperatures, which are very different from each other. The spectra at liquid He temperature show the line structure with the broad background in the low-frequency region. The frequencies of the line spectra are given in Table II together with those of the phosphorescence spectrum of naphthalene in the heptane and pentane matrix. The above two spectra correspond well to each other in the 0–0 band position and in vibrational structure. Therefore it is concluded that the phosphorescent state in the crystal is the naphthalene locally excited triplet state. Extra fine structure, thought to be due to the lattice vibrations, was observed for the crystal of the complex. The observation of lattice vibrations in the phosphorescence spectra may suggest that the emitting naphthalene is combined with the acceptor TCNB in the ground state and is not the extra naphthalene in crystal.

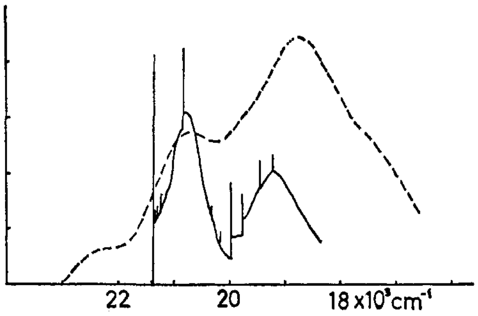

Figure 7. The phosphorescence spectra of the complex in crystalline state at 4.2°K (———) and 77°K (- - - -). The ordinate is the plate blackness.

Table II. Maximum Wavelengths (cm^{-1}) of the Phosphorescence Spectra

Complex crystal (liquid He)	Naphthalene in pentane[a] (liquid N_2)	Naphthalene in heptane[a] (liquid N_2)
21,340 s 0	21,268 s 0	21,277 vs 0
21,320 w 20		
21,270 w 70		
21,230 w 110		
20,820 m 520	20,756 w 512	20,767 m 510
	20,506 vw 762	20,517 vw 760
20,320 w 1020	20,250 w 1018	20,259 w 1018
20,160 w 1180		20,119 w 1158
19,960 m 1380	19,888 s 1380	19,896 s 1381
19,760 m 1580	19,688 s 1580	19,700 s 1577
19,450 w 1690		
	19,376 m 1892	19,386 m 1891
19,240 w 2100	19,175 m 2093	19,183 m 2094

[a] V. I. Mikhailenko, *et al.*, *Opt. Spectry.* (USSR), **20**, 29 (1966).

The spectra at liquid N_2 and H_2 temperatures are composed of broad bands, which appear in the same wavelength regions as those at liquid He temperature. Therefore the phosphorescence state at liquid N_2 and H_2 temperatures may also be related to the naphthalene triplet state, which is perturbed by the CT interaction. It is a problem why the complex crystal can emit the long-lived phosphorescence and why the temperature dependence of phosphorescence occurs. The most probable reason is that the emitting complexes are a type of traps in crystal.

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(27) J. Tanaka, *Bull. Chem. Soc. Japan*, **36**, 1237 (1963).

(28) For the sake of the elimination of the reabsorption, the emission of the thin layer of powder was observed. But at room temperature the emission of powder, which is made by crushing the crystal using an agate mortar, appears in longer wavelengths than that of the microcrystal as is shown in Figure 6. At liquid N_2 temperature, however, the emission of this powder is in agreement with that of the microcrystal. This unusual phenomenon of powder emission cannot be simply explained, though perhaps it may be related to the energy transfer to the surface traps. We could not obtain at room temperature the fluorescence spectra of crystal in which the reabsorption effects were completely eliminated.

(29) In solution we found the "excimer" type of fluorescence for some complexes. In TCNB-benzene, -toluene, and -mesitylene the fluorescence spectra at room temperature appear in the very long wavelength region, but at liquid N_2 temperature they have the mirror image relation with the absorption spectra. We will discuss the phenomena in more details in a future publication.