Charge-Transfer Interaction and Fluorescence in Some Tetracyanobenzene Complexes

Takayoshi KOBAYASHI, Keitaro YOSHIHARA,* and Saburo NAGAKURA

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo

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Fluorescence lifetimes and quantum yields were measured for some tetracyanobenzene complexes with benzene and its methyl derivatives, and the radiative and nonradiative rate constants were determined under various conditions. The results show that the low fluorescence intensities of the complexes in nonpolar fluid media are due to small radiative rate constants and that nonradiative processes become important for the complexes in polar fluid media. From the theoretical consideration of the observed radiative transition probability, it is found that the geometry and the charge distribution in the excited equilibrium state are greatly different from those in the excited Franck-Condon state for the complexes in fluid media at room temperature and that the degree of the charge-transfer in the former state amounts to 96—100%, while it is only 12—45% in the latter state. The stabilization energy due to the reorientation was obtained from the temperature dependence of the fluorescence spectrum.

The fluorescence spectra measured for charge-transfer (hereafter abbreviated to CT) complexes, though rather scanty,[1-9] have the following two characteristics: (1) their Stokes shifts in solution lie between 3500 cm^{-1} and 8500 cm^{-1} at low temperature (−190°C),[1,2] and (2) fluorescence has been observed for only a few CT complexes in solution at room temperature,[3-7] and its intensity is very weak even if it is observed.[10]

Short and Parker[4] determined the quantum yield of fluorescence at room temperature to be ~0.01 or less for the tetrachlorophthalic anhydride and pyromellitic dianhydride complexes with hexamethylbenzene and naphthalene in several solvents. Prochorow and Siegoczyński[5] also measured their fluorescence quantum yields and lifetimes in several solvents and obtained low quantum yields of less than 0.017. Mataga *et al.*[6,7] explained the decrease in the quantum yield with the solvent polarity as due to the decrease in the radiative transition probability. However, Prochorow and Siegoczyński[5] showed that the radiative transition probability might be constant for a series of solvents and that the radiationless transition probability increased with their dielectric constants, though they could not exclude the possibility that, in highly polar solvents, the radiative transition probability might diminish.

It must be emphasized that non-fluorescent CT complexes in fluid solutions at room temperature have fluorescence in the rigid phase.[1,2,11]

In order to explain the above-mentioned characters of CT complexes, we measured the fluorescence lifetimes and quantum yields of tetracyanobenzene complexes with benzene and its methyl derivatives, and determined the radiative and nonradiative rate constants under several conditions. On the basis of the observed results and the theoretical consideration of the radiative rate constants, we interpreted the low quantum yield and the large Stokes shift of CT fluorescence in terms of the reorientation of solvent molecules and the change in the geometry of the complex itself.

Experimental

Materials. Tetracyanobenzene (abbreviated hereafter to TCNB) used as an electron acceptor was purified by recrystallization from ethanol. Dotite spectrograde benzene and toluene were used as donors and solvents without further purification.[12] Commercially-available mesitylene and *m*- and *p*-xylene were purified by distillation. Durene was purified by repeated recrystallizations from benzene and by repeating zone refining about 50 times. Hexamethylbenzene (abbreviated hereafter to HMB) was purified by repeated recrystallizations from ethanol and thereafter by sublimation *in vacuo*.

Ethyl ether was shaken with a 10% aqueous sodium sulfite solution, washed with a saturated aqueous sodium chloride solution containing sodium hydroxide, dried over calcium chloride, and finally distilled over metallic sodium. Cyclo-

* Present address; The Institute of Physical and Chemical Research, Wako, Saitama.

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8) J. Czekalla, A. Schmillen, and K. J. Mager, *Ber. Bunsenges, Physik. Chem.*, **61**, 1053 (1957).
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10) The CT complexes which have hitherto been found to be fluorescent at room temperature are as follows:
Tetrachlorophthalic anhydride-substituted methylbenzenes[3,9]
Pyromellitic dianhydride-substituted methylbenzenes[3-5]
Tetracyanobenzene-some aromatic hydrocarbons[7].

11) J. Czekalla, A. Schmillen, and K. J. Mager, *Ber. Bunsenges. Physik. Chem.*, **63**, 623 (1959).

12) We checked, in the initial stage of our experiment, the effect of the purification of benzene and toluene upon fluorescence by comparing the results obtained by the use of the untreated materials with those obtained by the use of the materials purified by shaking with concentrated sulfuric acid, by washing, by drying, and finally by distillation. We could observe no significant effect of purification on the observed results.

hexane was shaken with fuming sulfuric acid, washed with water and aqueous sodium hydroxide, boiled with a mixture of fuming nitric acid and concentrated sulfuric acid, washed with the mixture more than three times, distilled with hydrochloric acid, washed with water, and dried with calcium chloride. After being passed through a newly activated silica gel column, it was finally distilled over metallic sodium.

Methyl methacrylate (MMA) was shaken with 5% aqueous sodium hydroxide several times until no color developed, washed with water more than five times, dried overnight with anhydrous magnesium oxide, and distilled under *ca.* 100 mmHg with nitrogen ebullition. Immediately after the distillation, it was passed through a column of activated silica gel covered with aluminum foil, and redistilled under reduced pressure with nitrogen ebullition. The purified MMA was stored at *ca.* −5°C and was used as a solvent and also as a material for the preparation of a polymer matrix as soon as possible after the above-mentioned purification.

Preparation of Polymer Rigid Solutions Containing Complexes. The rigid solutions of TCNB complexes in polymethyl methacrylate (PMMA) were prepared by polymerizing the MMA solutions in the following way. The MMA solution in a sample tube was deaerated carefully until no bubbling could be detected; then it was polymerized by being kept at 64°C in the dark for about 3 days, and finally slowly cooled to room temperature. No chemical change occurred during the polymerization in the electron donors and acceptors under consideration. We used transparent and completely polymerized rigid solutions with no crack at 77°K.[13] We carefully treated the polymerized samples in order not to expose them to light before measurements.

Measurements. The absorption spectra of TCNB complexes under various conditions were measured by a Cary recording spectrophotometer, Model 14 M. Emission spectra were measured by a JASCO CT-50 grating monochromator with a 100-W high-pressure mercury lamp at a light source, and by an Aminco-Bowman spectrophotofluorometer with a xenon or a mercury-xenon lamp. The emission was detected with an RCA 1P28, an RCA 1P21, or an EMI 9529A photomultiplier. The correct quantum spectra of the complexes were obtained by measuring the sensitivity spectrum of an optical system consisting of lenses, a monochromator, and a photomultiplier by the aid of a standard tungsten filament lamp. Fluorescence quantum yields, η_F's, were measured in the way described by Parker and Rees.[14] The fluorescence quantum yield of the tetrachlorophthalic anhydride-HMB complex was measured by taking the solution of quinine bisulphate in 0.1 N sulfuric acid as the standard. The value thus obtained is in good agreement with that measured by Prochorow and Siegoczyński[5] by using quinine bisulphate or trypaflavine as the standard. For the sake of convenience, the tetrachlorophthalic anhydride-HMB complex was adopted as the secondary standard in determining the quantum yields of the TCNB complexes under consideration, since its fluorescence and absorption are similar to those of the latter complexes in intensity, band shape, and position.

A nitrogen gas laser with a repetition rate of *ca.* 20 Hz, a peak power of ~20 kW, and a pulse width of ~3 nsec was used as the light source for the fluorescence-decay measurements.

Experimental Results

Absorption Spectra and Natural Lifetimes. Absorption spectra were measured for binary solutions containing TCNB in pure benzene, toluene, xylenes, and mesitylene, and also for MMA solutions containing TCNB as an electron acceptor and durene or HMB as an electron donor. The peak wave numbers (ν^A_{max}) and molar extinction coefficients (ε) for the observed CT bands are given in Table 1, together with the ionization potentials of the donors.[15] The natural lifetimes, τ_0's, and the corresponding radiative rate constants, k's, of the complexes were determined by the aid of Eq. (1) presented by Strickler and Berg[16]:

$$k(\mathrm{SB}) = \tau_0^{-1}(\mathrm{SB}) = 2.880 \times 10^{-9} n^2 \langle \nu^{F-3} \rangle_{Av}^{-1} \frac{g_l}{g_u} \int \varepsilon \, d\ln \nu^A \quad (1)$$

Here g_l and g_u represent the degeneracies of the lower and upper states, respectively; ν^A and ν^F are the wave numbers of the absorption and fluorescence spectra, respectively, and n is the refractive index of the solution. In actuality, k(SB) was obtained by the use of the refractive index of the solvent, n_0 instead of that of the solution. This may be expected to have no serious effect to the result, since the concentration of the solution is very small. The evaluated k(SB) values are given in Table 1.

Fluorescence Spectra, Stokes Shifts, Lifetimes, Quantum Yields, and Their Temperature Dependencies. Fluorescence spectra were measured under various conditions for the systems used for the absorption measurements. The total emission spectra are shown in Figs. 1 and 2. As clearly seen in Fig. 1, the fluorescence spectra measured at room temperature for the binary systems containing TCNB in benzene, toluene, *m*-

Table 1. The absorption peak wave number (ν^A_{max}), molar extinction coefficient (ε), and radiative rate constant (k) of TCNB complexes with various electron donors

Donor[a]	I[b] (eV)	n[c]	ν^A_{max} (10^3 cm^{-1})	ε (M^{-1} cm^{-1})	k(SB) (10^7 sec^{-1})
Benzene	9.245	1.5016	32.5	2200	3.8_4
Toluene	8.82	1.4893	31.8	1800	2.3_8
m-Xylene	8.45	1.4973	30.3	1540	1.3_9
p-Xylene	8.56	1.5004	30.5	1680	1.3_5
Mesitylene	8.39	1.4954	28.3	1400	1.1_1
Durene	8.03	1.5015	26.4[d]	660[d]	0.87_0
HMB	7.85	1.5015	24.6	880	0.80_0

a) The measurements were made for the binary systems including a small amount of TCNB in each donor except for the durene-TCNB and HMB-TCNB systems for which the MMA solutions were used.
b) The ionization potential of donor.
c) The refractive index of solvent.
d) The absorption spectrum of the TCNB-durene complex in MMA has no peak but a shoulder. The peak position was estimated by separating the absorption intensity in the concerned wavelength region into the two parts belonging to the strong and weak bands.

13) The incompletely polymerized solution was cracked at the liquid nitrogen temperature.
14) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).
15) The equilibrium constants for the CT complex formation were determined to be 0.79 and 2.8 ($l \cdot \mathrm{mol}^{-1}$) by the aid of the usual Stern-Volmer plot for the TCNB complexes with durene and HMB in MMA, respectively.
16) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

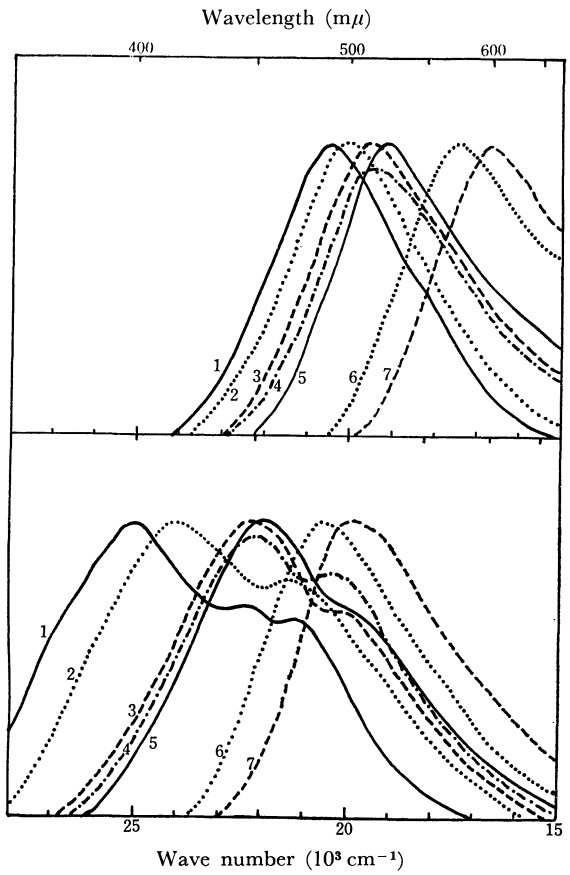


Fig. 1. The total emission spectra of TCNB complexes at room temperature (upper) and at 77°K (lower).

Curve	Donor	Solvent
1	benzene	benzene
2	toluene	toluene
3	*m*-xylene	*m*-xylene
4	*p*-xylene	*p*-xylene
5	mesitylene	mesitylene
6	durene	MMA
7	HMB	MMA

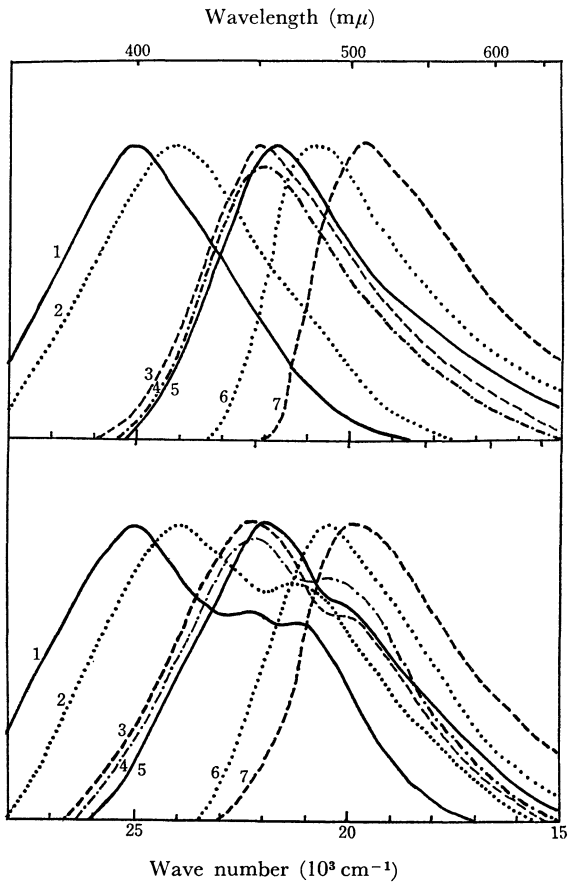


Fig. 2. The total emission spectra of TCNB complexes in PMMA solid solution at room temperature (upper) and at 77°K (lower). The numbering of the curves is the same as in Fig. 1.

xylene, *p*-xylene, and mesitylene (group I) and for the ternary systems of TCNB-durene-MMA and TCNB-HMB-MMA (group II) are different from those at the liquid nitrogen temperature. On the other hand, Fig. 2 shows that the fluorescence spectra of complexes in the PMMA rigid solution (group III) are essentially independent of the temperature, except for the fact that the CT phosphorescence appears at 77°K.

Tables 2 and 3 show the Stokes shifts observed for the TCNB complexes at room temperature and at 77°K, respectively. The observed values at 77°K lie between 8300 cm^{-1} for TCNB-*p*-xylene and 4500 cm^{-1} for TCNB-HMB-MMA, and are close to those previously observed for the other complexes *i.e.*, 8500 cm^{-1} for chloranil-1,2-benzanthracene and 3500 cm^{-1} for 1,3,5-trinitrobenzene-durene.[1,2] At room temperature, however, they are extraordinarily large; that is to say, they are 12000 cm^{-1} for TCNB-benzene

Table 2. The lifetime (τ_F), quantum yield (η_F), rate constans (k^F, k^{FQ}), and stokes shift ($\Delta(\nu^A_{max}-\nu^F_{max})$) at room temperature

Donor[a]	τ_F (nsec)	η_F	k^F (10^5 sec^{-1})	k^{FQ} (10^6 sec^{-1})	ν^F_{max}	ν^{00} [b]	Δ^{00}_{FC} [c]	$\Delta(\nu^A_{max}-\nu^F_{max})$
					(10^3 cm^{-1})			
Benzene	147±3	0.09±0.02	6.1±2.2	6.2±0.3	20.5	23.5	3.0	12.0
Toluene	122±3	0.08±0.02	6.5±1.8	7.5±0.4	20.0	23.0	3.0	11.8
m-Xylene	53±2	0.02±0.01	3.8±2.0	15±3	19.6	22.0	2.4	10.7
p-Xylene	52±2	0.02±0.01	3.9±2.1	15±4	19.6	21.8	2.2	10.9
Mesitylene	43±2	0.01±0.005	2.3±1.3	23±2	19.2	21.5	2.3	9.1
Durene	8±1	0.0003±0.0001	0.38±0.18	120±20	17.2	19.8	2.6	9.2
HMB	5±1	~0.0001	~0.2	~200	16.7	19.0	2.3	7.9

a) See footnote a) in Table 1.
b) The number of 0-0 transition band of fluorescence at room temperature.
c) $\Delta^{00}_{FC}=\nu^{00}-\nu^F_{max}$

TABLE 3. THE LIFETIME (τ_F), QUANTUM YIELD (η_F), RATE CONSTANTS (k^F, k^{FQ}), FREQUENCY DIFFERENCE (Δ^{00}_{FC}) AND STOKES SHIFT ($\Delta(\nu^A_{max}-\nu^F_{max})$) AT 77°K

Donor[a]	τ_F (nsec)	η_F	k^F (10^6 sec^{-1})	k^{FQ} (10^6 sec^{-1})	ν^F_{max} (	ν^{00}[b]	Δ^{00}_{FC}	$\Delta(\nu^A_{max}-\nu^F_{max})$)
					10^3 cm^{-1}			
Benzene	38±3	0.63±0.05	17	9.5	25.0	27.5	2.5	6.5
Toluene	50±3	0.55±0.05	11	9.0	23.8	26.5	2.7	8.0
m-Xylene	74±3	0.51±0.05	6.9	6.6	22.2	25.0	2.8	8.1
p-Xylene	72±3	0.46±0.05	6.4	7.5	22.2	25.0	2.8	8.3
Mesitylene	85±3	0.47±0.05	5.5	6.5	22.0	24.7	2.7	6.3
Durene	58±3	0.25±0.05	4.3	13	20.4	22.8	2.4	6.0
HMB	39±3	0.16±0.05	4.1	22	20.1	21.8	1.7	4.5

a) See footnote a) in Table 1.
b) The wave number of the 0-0 transition band of fluorescence at 77°K.

and 7900 cm^{-1} for TCNB-HMB-MMA. These facts suggest that the equilibrium state of the lowest excited state is very different from the Franck-Condon state.

The quantum yields were determined at room temperature for the complexes of groups I and II, but at the liquid nitrogen temperature they could not be measured because all the samples except for the TCNB-toluene system became opaque. Therefore, the quantum yields of the complexes of groups I and II at the liquid nitrogen temperature are assumed to be equal to the value of the corresponding TCNB complexes of group III at the same temperature. The validity of this assumption was checked by comparing the fluorescence intensity at 77°K measured for the TCNB-toluene-PMMA system with that for the TCNB-toluene system, which vitrifies in a thin glass tube. The quantum yields derived from the integrated fluorescence intensities observed for the TCNB-toluene and TCNB-toluene-PMMA systems deviate from each other by only 15%. Radiative and nonradiative rate constants were obtained from the quantum yields and lifetimes measured at room temperature and at 77°K; they are listed in Tables 2 and 3.

The fluorescence lifetimes and quantum yields were measured at various temperatures between 77°K and 300°K for the TCNB-toluene and TCNB-HMB-PMMA systems, and their radiative and nonradiative rate constants were obtained; the results are shown in Figs. 3 and 4, together with the temperature dependencies of the wave numbers of the fluorescence maxima, the lifetimes, and the quantum yields. According to Figs. 3 and 4, TCNB-toluene and TCNB-HMB-PMMA show greatly different temperature dependencies of the fluorescence maxima, lifetimes, quantum yields, and radiative rate constants. These quantities change abruptly at about 140°K for the former, while for the latter they vary continuously and the change is small in the whole temperature range.

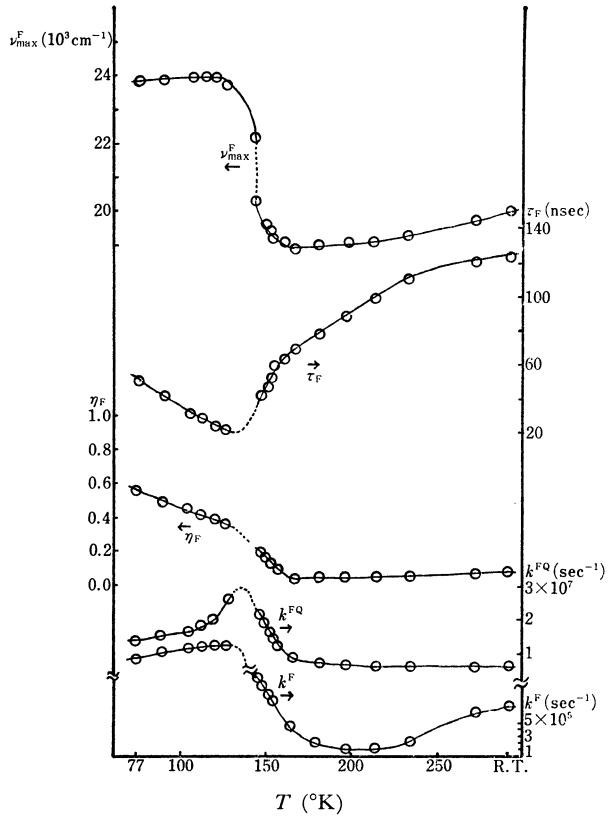


Fig. 3. Temperature dependence of fluorescence maximum (ν^F_{max}), lifetime (τ_F), quantum yield (η_F), and rate constants (k^F, k^{FQ}) for TCNB-toluene.

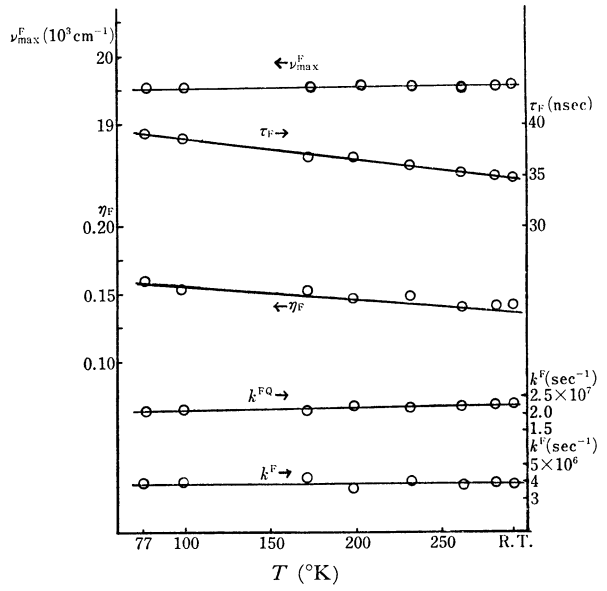


Fig. 4. Temperature dependence of fluorescence maximum (ν^F_{max}), lifetime (τ_F), quantum yield (η_F), and rate constants (k^F, k^{FQ}) for TCNB-HMB-PMMA.

Table 4. The fluorescence maxima (ν^F_{max}), lifetimes (τ_F) quantum yields (η_F), and rate constants (k^F, k^{FQ}) of some TCNB complexes under several conditions

Donor	Solvent	Temp. °C	ν^F_{max} (10^3 cm^{-1})	η_F	τ_F (nsec)	k^F (10^5 sec^{-1})	k^{FQ} (10^7 sec^{-1})
Benzene	Benzene	80	20.5		52		
m-Xylene	*m*-Xylene	−72	19.4		18		
p-Xylene	*p*-Xylene	−72	22.2		70		
Durene	Durene	80	19.0		25		
	Cyclohexane	23	19.0	0.0006	17	0.35	5.9
	Ethyl ether	23	17.2	0.0003	8	0.38	12
	Ethyl ether	74	17.2	0.0002	6	0.33	17
HMB	Cyclohexane	23	18.0	~0.00027	12	~0.2	8.3
	Benzene	23	16.7	~0.00023	11	~0.2	9.1
	MMA	23	16.7	~0.0001	5	~0.2	20
	Ethyl ether	23	16.7	~0.0001	5	~0.2	20

Tables 2, 3, and 4 show that the lifetime of the TCNB-*p*-xylene system at the dry ice-ethanol temperature (−72°C) is close to that at 77°K, while in the TCNB-*m*-xylene system the values at both temperatures are different. This is related to the difference in the rigidity of the solutions. At both temperatures, the TCNB-*p*-xylene system is in a rigid state and has a similar lifetime. The TCNB-*m*-xylene system is fluid at dry ice-ethanol temperature and the lifetime at this temperature is shorter than that at 77°K.

Fluorescence Lifetime and Quantum Yield in Polar Solvents. The fluorescence maxima, lifetimes, and quantum yields of several TCNB complexes were measured in various solvents; the results for the TCNB-durene and TCNB-HMB systems are shown in Table 4. This table shows that the fluorescence lifetimes τ_F's, are shorter in polar solvents than in nonpolar solvents. However, the radiative rate constant, $k_F=\eta_F/\tau_F$, for each complex is nearly independent of the solvents used. The situation is the same for the other complexes, though the details will not be presented here.

CT Complexes in the Crystalline State. The fluorescence maximum wave numbers, lifetimes, and relative intensities, I_F's for the TCNB-durene and TCNB-HMB complexes in the crystalline state are given in Table 5. The fluorescence maximum wave numbers and lifetimes given in this table are similar to those of the corresponding complexes in PMMA or in solution at 77°K. The slight difference in the fluorescence maximum wave number between room temperature and 77°K was found by careful measurements to be due to the enhancement of the reabsorption at the higher temperature. The τ_F/I_F values are almost constant between room temperature and 77°K; therefore, the radiative rate constants are almost independent of the temperature.

Table 5. Fluorescence maximum wave numbers (ν^F_{max}), lifetimes (τ_F), and relative intensities (I_F) of the TCNB complexes with durene and hexamethylbenzene in crystalline state

Donor	Temp.	ν^F_{max} (10^3 cm^{-1})	τ_F (nsec)	I_F
Durene	R.T.	20.8	34	1
	77°K	20.4	32	1.1
HMB	R.T.	19.2	26	1
	77°K	19.0	40	1.5

Theoretical Consideration and Discussion

The Possibility of 1 : m Complexes in the Excited State. The large Stokes shift observed for the complexes in the fluid state may be explained by the reorientation of the solvent and solute molecules or by 1 : *m* ($m\geq 2$) complex (AD_m) formation in the excited state. According to Table 4, the binary system, for example, TCNB-durene at 80°C, has the fluorescence peak at 19.0×10^3 cm^{-1}. This position is almost the same for the solution containing TCNB-durene in an inert solvent like cyclohexane. This seems to mean that the large Stokes shift for this system in fluid media is not due to the 1 : *m* complex formation in the excited state. The situation is the same for the other systems showing a large Stokes shift in fluid media.

Dependence of the Fluorescence Spectrum on the Rigidity of the Medium. The large Stokes shifts observed for fluorescence spectra in fluid solutions are conceivably caused by the stabilization due to the interaction of the excited CT complex with a large dipole moment with the surrounding solvent molecules.[17]

According to Bakshiev, with a decrease in the temperature the fluorescence spectra of polyatomic molecules shift first toward the longer wavelengths and thereafter toward the shorter wavelength as the solvent viscosity increases.[17] Accordingly, a turning point is expected to be observed for the ν^F_{max} *versus* temperature curve. This effect was in fact observed with the TCNB-toluene system, as is shown in Fig. 3. The turning point at ~140°K is close to the melting point of the toluene solution containing 10^{-3} M of TCNB. This tendency has been found for several systems with intramolecular CT interaction, such as biphenyl, stilbene, and fluorene derivatives in various

17) a) N. G. Bakshiev, *Opt. i Spektroscopiya*, **16**, 821 (1964); *Opt. Spectry.*, **16**, 446 (1964). b) N. G. Bakshiev, *Opt. i Spektroscopiya*, **20**, 976 (1966); *Opt. Spectry.*, **20**, 542 (1966).

solvents.[18]

From Eq. (4) in Reference (17b) and the fluorescence and absorption maxima observed by us and in the literature,[7] we estimate the dipole moment in the excited state of the TCNB-HMB complex to be 8.34 D, by assuming the Onsager radius to be 5.81 Å.[19] This value is rather small compared with 14(±3)D or 10(±1.5)D of the tetrachlorophthalic anhydride-HMB complex.[9,20]

We can now roughly estimate the stabilization energy due to the reorientation of the solute and solvent molecules in the excited state (E_R), the Franck-Condon energies in the ground state before and after reorientation (E_{gb}^{FC} and E_{ga}^{FC}, respectively), and the Franck-Condon energy in the excited state (E_e^{FC}). Their definitions and relations to the wave numbers of the absorption and fluorescence maxima are shown in Fig. 5, while their values are listed in Table 6.

The potential energy curves of the ground and excited states before and after reorientation are shown in Fig. 5, where q means a set of the coordinates which indicates the positions and orientations of the solvent molecules near the solute CT complex. All the q_G's and q_E's adjust themselves to minimize the energies of the ground state, $E_G(R, Q, q)$, and the lowest excited state, $E_E(R, Q, q)$, respectively. Fluorescences in rigid and fluid media take place from the lowest point of the

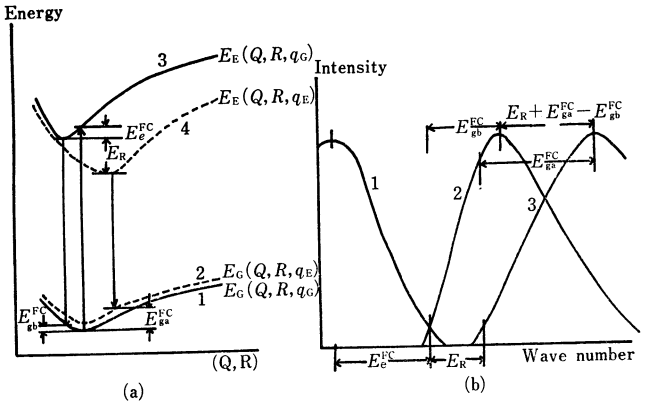


Fig. 5. (a) The potential energy curves of CT complexes. The curves are drawn by plotting the energies *versus* the internal coordinates of the component molecules, Q's and the coordinates concerning the intermolecular distance and orientation, R's. Coordinates of surrounding solvent molecules, q's are determined in such a way as to minimize the energy for a fixed point of the abscissa. 1, ground state before reorientation; 2, ground state after reorientation; 3, first excited singlet state before reorientation; 4, first excited singlet state after reorientation.
(b) The absorption and fluorescence spectra of the CT complex. 1, absorption; 2, fluorescence before reorientation; 3, fluorescence after reorientation.

Table 6. THE FRANCK-CONDON DESTABILIZATION ENERGIES IN THE EXCITED AND GROUND STATES (E_e^{FC} AND E_g^{FC}, RESPECTIVELY) AND THE REORIENTATION STABILIZATION ENERGY (E^R) (10^3 cm^{-1})

Donor[a]	ν_{max}^F(77°K) $-\nu_{max}^F$(RT)	E_{ga}^{FC}	E_{gb}^{FC}	E_e^{FC}	E_R
Benzene	4.5	3.0	2.5	5.0	4.0
Toluene	3.8	3.0	2.7	5.3	3.5
m-Xylene	2.6	2.4	2.8	5.3	3.0
p-Xylene	2.6	2.2	2.8	5.5	3.2
Mesitylene	2.8	2.3	2.7	3.6	3.2
Durene	3.2	2.6	2.4	3.6	3.0
HMB	3.4	2.3	1.7	2.8	2.8

a) See footnote a) in Table 1.

$E_E(R, Q, q_G)$ and $E_E(R, Q, q_E)$, respectively. The stabilization energy due to the reorientation, E_R, is defined as the energy difference between the two lowest points of the two potential energy curves.

As is shown in this table, the E_R value increases with an increase in the ionization potentials of donors. This may be related to the experimental fact that the difference in the radiative rate constant between room temperature and 77°K increases with the increase in the ionization potential of the donor.

Radiative and Nonradiative Rate Constants. The complexes in a rigid solution, in a nonpolar fluid medium, and in a polar fluid medium are denoted as the complexes in the A, B, and C states, respectively. According to Tables 2, 3, and 4, the radiative rate constants are 10^{6-7} sec^{-1} and 10^{4-5} sec^{-1} for the complexes in the A and B states, respectively. Furthermore, these tables show that the nonradiative rate constants of complexes in the A and B states are 10^{6-7} sec^{-1}, while those in the C state are about 10^8 sec^{-1}. From these facts, it can be concluded that the low fluorescence intensity of the CT complexes in a nonpolar fluid medium is due to the small radiative rate constant and that, for the CT complexes in a polar fluid medium, the nonradiative quenching effect becomes important in addition to the above-mentioned effect. Therefore, it may be said that the discussions made by Mataga and Murata[7] and by Prochorow and Siegoczyński[5] concerning the low fluorescence intensity are correct for the CT complexes in nonpolar and polar media, respectively.

When we compare the radiative rate constant, k(SB), in Table 1, obtained from the absorption intensity, with the rate constant, k^F, in Tables 2 and 3, we can see that the former is larger than the latter for each complex, both at room temperature and at the liquid nitrogen temperature.[21] In particular, the value of k^F at room temperature is extraordinarily small compared with k(SB). This fact, as will be described below, can be explained by considering the great differences in the electron distribution and in the

18) E. Lippert, W. Luder, and F. Moll, *Spectrochim. Acta*, **10**, 585 (1959).

19) The value is given by $(\sqrt{1.7^2+3.96^2}+1.5)$ Å, where 1.7 Å, 3.96 Å, and 1.5 Å are a half of the intermolecular distance, the distance between the center of the TCNB molecule and one of its nitrogen atoms, and the van der Waals radius of nitrogen, respectively.

20) J. Czekalla, *Z. Elektrochem.*, **64**, 1221 (1960); *Chimia* (Switz.), **15**, 26 (1961).

21) Mataga and Murata[7] obtained larger natural lifetimes, 50 and 60 nsec for TCNB-benzene and TCNB-toluene, respectively, than the corresponding values obtained by us, 26 and 43 nsec, respectively. According to our opinion, their values are too great because they disregarded the n^2 in Eq. (1) in their evaluation.

Table 7. The observed and calculated rate constants and the contributions of the CT configuration to the excited state at 77°K and at room temperature (RT)

Donor	$I-A$ (eV)	CT(%) 77°K	k(calc) (10^6 sec^{-1})	k(SB) (10^6 sec^{-1})	$k^F_{77°K}$ (10^6 sec^{-1})	CT(%) RT
Benzene	8.845	12.4	26.0	38.4	17	96.7
Toluene	8.42	19.4	18.6	23.8	11	96.7
m-Xylene	8.16	28.7	14.7	13.9	6.9	98.1
p-Xylene	8.045	30.1	14.8	13.5	6.5	98.1
Mesitylene	7.99	32.2	11.8	11.1	5.6	99.7
Durene	7.63	41.2	8.38	8.70	4.4	99.8
HMB	7.45	44.6	6.14	8.00	4.0	99.9

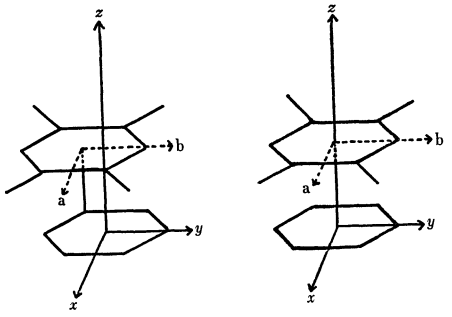
geometrical configuration between the Franck-Condon state and the excited equilibrium state.

The Calculations of the Radiative Rate Constants and the Contribution of the CT Configuration to the Excited State. The wave functions and energies of the ground and excited states of the complex were calculated by considering the configuration interaction among the ground, CT, and locally-excited (abbreviated hereafter to LE) configurations[22,23] constructed by putting electrons into the SCF of MO's of TCNB and benzene. The actual calculations were made by an electronic computer, FACOM 270—30.

The calculations for the system in the rigid solvent were made for the geometrical structure shown in Fig. 6(a), the most stable geometry in the ground state,[24] the ionization potential of the electron donor, I, being taken as a parameter and the electron affinity of the electron acceptor, A, being fixed at 0.4 eV.[25]

By evaluating the matrix element of the dipole moment by the aid of the Mulliken approximation and by taking the diagonal element concerning the CT configuration and the off-diagonal element between the ground and LE configurations to be 3.4 Å and 0.3 Å, respectively, we calculated the transition moment and the natural radiative rate constant, k, which corresponds to k(SB) in Table 1. The results are shown in Table 7. For purposes of comparison, k(SB) and k^F at 77°K ($k^F_{77°K}$) are also tabulated in this table. The k values calculated for the complexes under consideration lie intermediate between the corresponding k(SB) and $k^F_{77°K}$ values. Generally speaking, the calculated k value agrees well with the observed k(SB) or $k^F_{77°K}$ value for each complex. The contribution of the CT configuration to the excited Franck-Condon state changes from 12.4% for the TCNB-benzene complex to 44.6% for the TCNB-HMB complex.

Now let us consider the energy of the lowest excited singlet state in its potential energy minimum. There is no available data on the most stable configuration in the excited state, so we calculated its energy by the method described in the previous paper[23] for various geometrical configurations; the results are shown in Fig. 7. The energy contour map for the lowest excited state shown in this figure was obtained by locating the plane of TCNB parallel to that of benzene with a distance of 3.4 Å and by setting, as is shown in Fig. 6, the a axis of the TCNB molecule parallel to the x axis. It may be worth noting that the main feature in the



(a) (b)

Fig. 6. The geometrical configuration of the CT complex.
(a) stable configuration in the ground state.
(b) stable configuration in the first excited state.
The distance between the two benzene rings is taken to be 3.4Å.

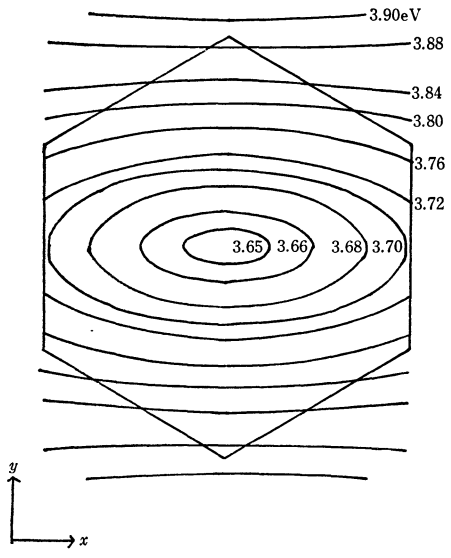


Fig. 7. The energy contour map for the lowest excited singlet state of the TCNB-benzene complex.

22) S. Iwata, J. Tanaka, and S. Nagakura, *J. Amer. Chem. Soc.*, **88**, 894 (1966).
23) T. Kobayashi, S. Iwata, and S. Nagakura, This Bulletin, **43**, 713 (1970).
24) The geometry shown in Fig. 6(a) is very similar to that determined for the TCNB-durene and TCNB-HMB crystals by the X-ray diffraction technique (TCNB-durene: H. Tsuchiya, N. Niimura, and Y. Saito, private communication; TCNB-HMB; N. Niimura, Y. Ohashi, and Y. Saito, This Bulletin, **41**, 1815 (1968)).
25) G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, **3**, 617 (1964).

energy contour map is common for all the TCNB complexes examined and that in the most stable configuration, the component molecules are located with their centers on the z axis, as is shown in Fig. 6(b).

From the above-mentioned facts, it may be expected that, in fluid media, the component molecules reorient to a great extent and take the geometrical configuration shown in Fig. 6(b). Furthermore, there occur reorientations of the surrounding solvent molecules[26] in addition to those of the electron donor and acceptor molecules. Next, we will describe the wave functions of the ground and excited states of the reoriented system in general forms.

$$\theta_{re}^{G} = a_0^{re}\theta_0(AD)_{re} + \sum_i a_i^{re}\theta_i(A^-D^+)_{re} + \sum_j a_j^{re}\theta_j(A^*D)_{re} \quad (2)$$

$$\theta_{re}^{E} = b_0^{re}\theta_0(AD)_{re} + \sum_i b_i^{re}\theta_i(A^-D^+)_{re} + \sum_j b_j^{re}\theta_j(A^*D)_{re} \quad (3)$$

where θ_0, θ_i's, and θ_j's are the wave functions of the ground, CT, and LE (in acceptor) configurations, respectively, where a_m's and b_m's are the coefficients of the corresponding configurations in the ground and excited states, respectively, and where the superscript or subscript "re" means that the wave function or coefficient is connected with the reoriented system.

In the geometry shown in Fig. 6(b), the overlap integral between electron-donating and -accepting orbitals is equal to zero because of the high symmetricity of the system.[27] This means that the a_i^{re}, a_j^{re}, and b_0^{re} coefficients are nearly equal to zero[28] and that the matrix element, $\langle\theta_i(A^-D^+)_{re}|\vec{er}|\theta_0(AD)_{re}\rangle$, is very small. Here, r represents the coordinate of an electron. Thus, only the following term contributes to k_{RT}^{F};

$$\sum_j a_0^{re}b_j^{re}\langle\theta_0(AD)_{re}|\vec{er}|\theta_j(A^*D)_{re}\rangle \quad (4)$$

where $a_0^{re}\cong 1$. The transition-moment integral in Eq. (4) can be estimated by the aid of the observed absorption spectrum of TCNB itself.

From the observed k^F values at room temperature (k_{RT}^{F}) given in Table 2 and the matrix element shown by Eq. (4), we can obtain the coefficient of the lowest LE (in the acceptor), b_1, which is dominant among b_j's; therefore, we can evaluate the contributions of the LE and CT configurations to the fluorescent state after reorientation. The evaluated values for the CT configuration are given in Table 7. This table shows that, even for the TCNB-benzene and TCNB-toluene complexes, for which the contributions of the CT configuration are less than twenty percent in the Franck-Condon states, they exceed 95% in the excited equilibrium state after reorientation at room temperature. This conclusion as to the TCNB-toluene system is consistent with the result obtained by Masuhara and Mataga from the measurement of the absorption due to the transition from the first excited singlet state to the higher excited state.[29] It is worthy of notice that the degree of the CT between electron donor and acceptor changes greatly upon the reorientation of the component molecules of the complex and of the solvent molecules.

The experimental results given in Table 4 show that the decrease in the fluorescence intensity in a polar solvent is due to the increase in the nonradiative decay. This seems to mean that the scarcity of fluorescence at room temperature for the CT complex in a polar solvent may be due to the rapid nonradiative decay. In view of the great contribution of the CT configuration to the excited equilibrium state after reorientation, the rapid nonradiative process in a polar solvent may be the dissociation process into ions. On the other hand, the scarcity of fluorescence at room temperature for the CT complex in a nonpolar solvent can be mainly due to the small radiative rate constant, as has been described above.

26) In actuality, it is difficult to evaluate the wave functions including surrounding solvent molecules. Therefore, we do not intend to obtain the actual forms of the wave functions from theoretical calculations, alone.

27) The overlap integral between electron-donating and accepting orbitals may be small even when the geometrical configuration of the reoriented system deviates slightly from that shown in Fig. 6(b). This is because the distance between the two component molecules is increased by the increase in the solution energy caused by the reorientation of the solvent molecules.

28) Since $\theta_j(A^*D)_{re}$'s and $\theta_0(AD)_{re}$ mix only through $\theta_i(A^-D^+)_{re}$'s, a_j's are also equal to zero when a_i's vanish.

29) H. Masuhara and N. Mataga, *Chem. Phys. Lett.*, **6**, 608 (1970).