A Photo-selection Study of the Charge-transfer Phosphorescence

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The polarization of the charge-transfer phosphorescence has been studied by the method of photo-selection. It has been measured relative to the electric vector of the excitation light corresponding to the charge-transfer band in wavelength for the complexes of tetracyanobenzene, *o*-, *m*-, and *p*-dicyanobenzenes, tetrachlorophthalic anhydride, and phthalic anhydride as electron acceptors, and methyl-substituted benzenes as electron donors, in organic glass at 77 K. It has been shown that the degree of polarization through excitation into the charge-transfer band is almost constant in the phosphorescence region, while it gradually decreases as the ionization potential of the donor increases for any of the acceptors. These observations can reasonably be interpreted in terms of a model in which the charge-transfer phosphorescence is polarized normal to the molecular plane, irrespective of the complex, and in which the change in the polarization degree of the charge-transfer phosphorescence is responsible for the change in the direction of the transition moment of the charge-transfer absorption band.

Phosphorescences of molecular complexes different from those of the constituent molecules themselves were observed by Iwata *et al.* for the complexes containing tetracyanobenzene (TCNB), phthalic anhydride (PA), tetrachlorophthalic anhydride (TCPA), and pyromellitic dianhydride as electron acceptors and methyl-substituted benzenes as electron donors.[1] These phosphorescences were ascribed to the phosphorescence from the lowest triplet state of the complex with the charge-transfer character. Hayashi *et al.* observed the ESR spectra of the phosphorescent triplet states of the TCNB, *o*-dicyanobenzene(*o*-DCNB), *m*-DCNB, and *p*-DCNB complexes and determined the contribution of the charge-transfer character in the lowest triplet states from an analysis of the observed fine structure constants.[2-4]

It seemed that it would be interesting to clarify the S-T mixing mechanism in the triplet states of these complexes. Kobayashi *et al.* studied energy-transfer processes involving the triplet states of TCNB complexes and estimated the contribution of the phosphorescence state from the phosphorescence radiative rate constant.[5] Tsujino *et al.* confirmed that the TCNB complexes in the phosphorescent state are produced directly from the excited Franck-Condon state.[6] We ourselves tried to apply the photo-selection method to the charge-transfer phosphorescence in order to obtain some information on this problem. In this paper the experimental results of the polarization of the charge-transfer phosphorescence will be presented, and the nature of the charge-transfer triplet state of these complexes and also that of the lowest excited charge-transfer singlet state will be discussed.

Experimental

The phosphorescence spectra and their polarizations were measured by means of an apparatus described previously.[7] The degree of polarization was calculated using this formula:

$$P = \frac{I_{//} - I_{\perp}}{I_{//} + I_{\perp}}$$

in which $I_{//}$ and $I_{\perp}$ refer to the intensities of the emitted light polarized parallel to and perpendicular to the exciting light respectively.

All the measurements were carried out at 77 K in an ether-isopentane(EP) (1 : 1 volume ratio) or an ethanol glass solution, the concentrations of the samples being 10^{-2}—10^{-4} M of the donor and 10^{-3}—10^{-5} M of the acceptor. The sample was transferred into a Pyrex cell, degassed, and sealed off.

The absorption spectra were measured at room temperature by a Shimadzu MPS-50L spectrophotometer.

Benzene, *p*-xylene, and mesitylene were of a reagent grade and were purified further through distillation under reduced pressure. Durene of an u.p. grade supplied by the Tokyo Kasei Co. was used without purification. Hexamethylbenzene(HMB), TCPA, PA, *o*-DCNB, *m*-DCNB, and *p*-DCNB were repeatedly recrystallized from ethanol and sublimed *in vacuo*. TCNB was prepared according to Lawton *et al.*[8] and was purified through recrystallization from ethanol several times. Ether, isopentane, and ethanol were carefully purified by modifications of methods described in a book by Kuwata.[9]

Results

The phosphorescence spectra of the TCNB-HMB complex in ethanol obtained by the excitation of the Hg 405 nm and TCNB obtained by the excitation of the Hg 313 nm line are shown in Fig. 1, together with the absorption spectra of TCNB, HMB, and the TCNB-HMB complex in an ethanol solution. Figure 2 illustrates the degree of polarization, *P*, of the phosphorescence of the TCNB-HMB complex analyzed at 540 nm plotted as a function of the excitation wavelength. It is shown that the polarization measured in the charge-transfer absorption region is nearly constant within the limits of experimental error. The *P* values of the phosphorescence excited in the local excitation region are smaller than those excited in the charge-transfer band. Figure 3 shows that the polarization degree measured by the excitations at 436, 365, and 313 nm depends upon the wavelength of the phosphorescence spectrum. It is found that the polarization is roughly constant throughout the region of the phosphorescence spectrum obtained by excitation with the charge-transfer band. It may be concluded from Figs. 2 and 3 that the degree of polarization relative to the charge-transfer band is about 0.4. This value indicates that the transition moment of the phosphorescence is nearly parallel to that of the charge-transfer

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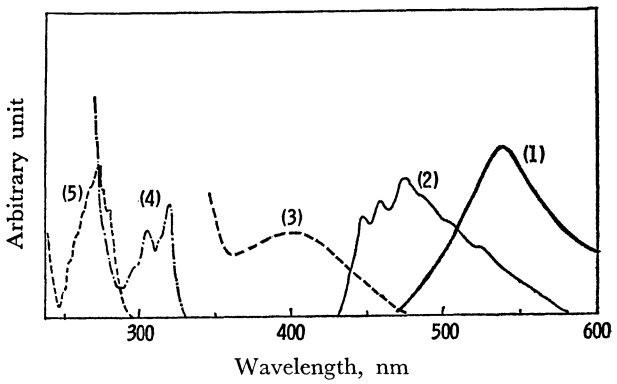

Fig. 1. Phosphorescence and absorption spectra of TCNB, HMB and TCNB-HMB complex in ethanol solution: (1) Phosphorescence spectrum of TCNB-HMB complex at 77 K (uncorrected to photomultiplier sensitivity); (2) Phosphorescence spectrum of TCNB at 77 K (uncorrected to photomultiplier sensitivity); (3) Charge-transfer absorption band; (4) Absorption Spectrum of TCNB; (5) Absorption spectrum of HMB.

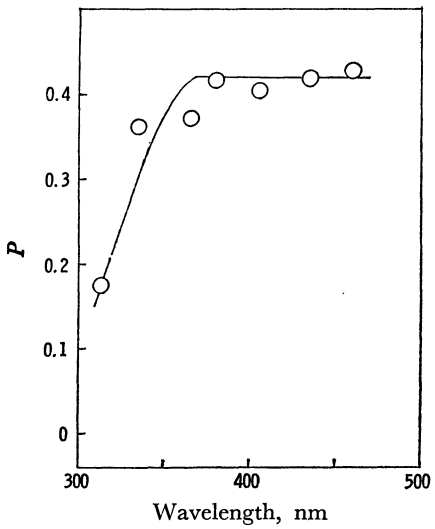

Fig. 2. Variation of the degree of polarization of TCNB complex analyzed at 540 nm with the wavelength of excitation.

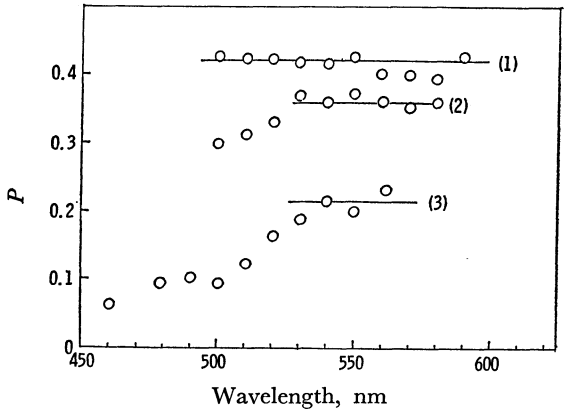

Fig. 3. Phosphorescence polarization of TCNB-HMB complex as obtained by excitation at various wavelengths: (1) 436 nm; (2) 365 nm; (3) 313 nm.

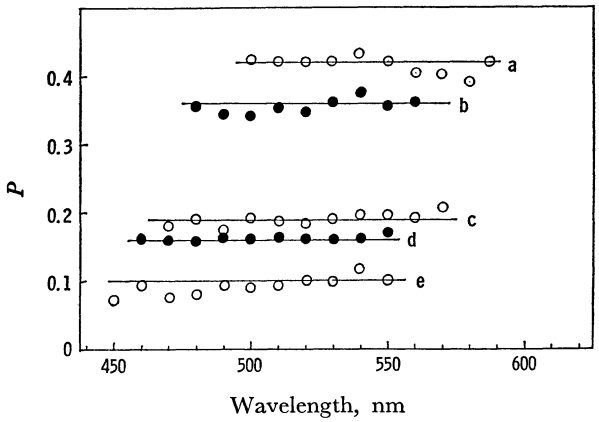

Fig. 4. Phosphorescence polarization of TCNB complexes with excitation into the charge-transfer band; (a) TCNB-HMB, (b) TCNB-durene, (c) TCNB-mesitylene, (d) TCNB-*p*-xylene, and (e) TCNB-benzene.

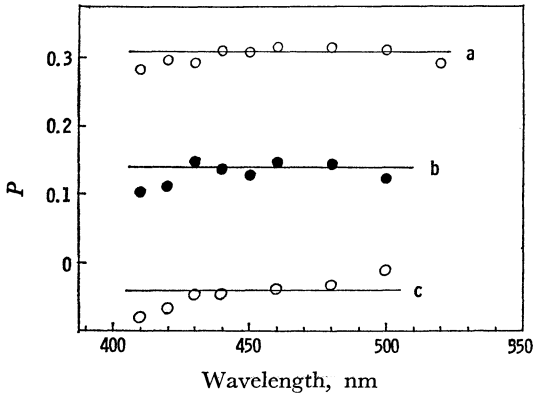

Fig. 5. Phosphorescence polarization of *o*-DCNB complexes; (a) *o*-DCNB-HMB, (b) *o*-DCNB-durene, and (c) *o*-DCNB-mesitylene.

band and that the phosphorescence is, therefore, polarized mostly perpendicular to the molecular plane. Being influenced by the uncomplexed TCNB molecules and/or some other impurities, the *P* values gradually decrease in the shorter-wavelength region of the phosphorescence obtained by excitation at 365 and at 313 nm, as is shown in Fig. 3. Similar behavior of the phosphorescence polarization was also observed for all the other complexes upon excitation into the S-S transition region of the constituent molecules.

Figure 4 compares the polarization of the phosphorescences of the TCNB complexes with HMB, durene, mesitylene, *p*-xylene, and benzene in an ethanol solution relative to the excitation of the molecule to the charge-transfer band. The polarizations were found to be nearly constant throughout the phosphorescence region for any of the complexes. Furthermore, it is apparent that the degree of polarization increases as the number of the CH_3-radical of the donor increases from benzene to HMB.

Similar results were also obtained for the *o*-DCNB, *m*-DCNB, *p*-DCNB, TCPA, and PA complexes with methylated benzenes; they are shown in Figs. 5—9

Table 1. Polarization degrees of TCNB complexes and ionization potentials of donors

Donor	P						I_p (eV)
	TCNB	*o*-DCNB	*m*-DCNB	*p*-DCNB	TCPA	PA	
HMB	0.4_2	0.3_1	0.2_6	0.2_2	0.1_8	0.3_2	7.85
Durene	0.3_6	0.1_4	0.1_2	0.1_1	0.1_6	0.1_0	8.03
Mesitylene	0.1_9	-0.0_4	-0.0_4	-0.0_3	0.0_5	0.0_5	8.39
p-Xylene	0.1_6				0.0_4		8.445
Benzene	0.1_0						9.245

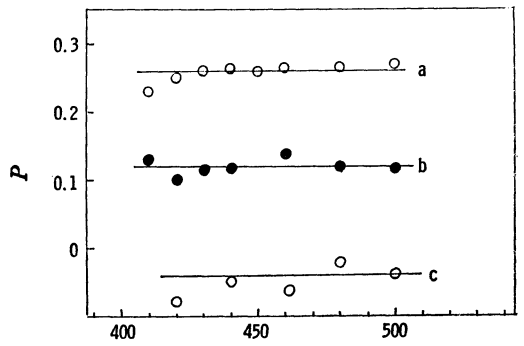

Fig. 6. Phosphorescence polarization of *m*-DCNB complexes; (a) *m*-DCNB-HMB, (b) *m*-DCNB-durene, and (c) *m*-DCNB-mesitylene.

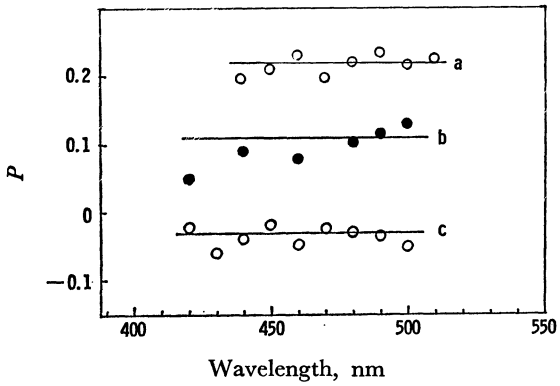

Fig. 7. Phosphorescence polarization of *p*-DCNB complexes; (a) *p*-DCNB-HMB, (b) *p*-DCNB-durene, and (c) *p*-DCNB-mesitylene.

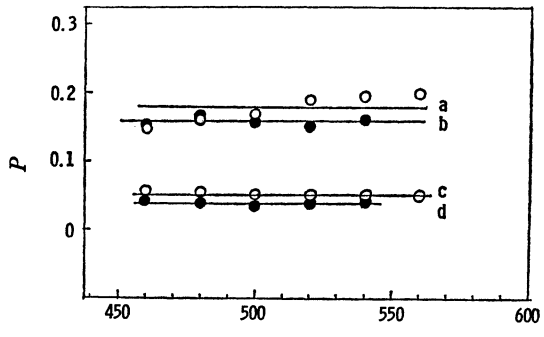

Fig. 8. Phosphorescence polarization of TCPA complexes; (a) TCPA-HMB, (b) TCPA-durene, (c) TCPA-mesitylene, and (d) TCPA-*p*-xylene.

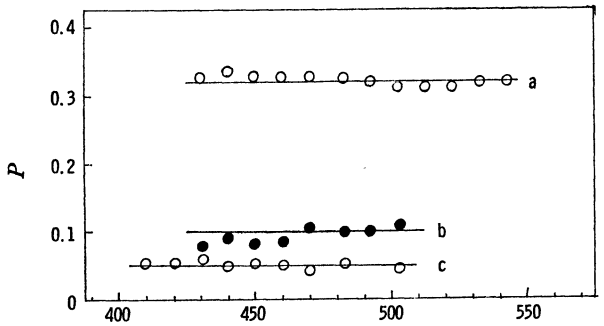

Fig. 9. Phosphorescence polarization of PA complexes; (a) PA-HMB, (b) PA-durene, and (c) PA-mesitylene.

respectively.

Table 1 summarizes and compares the polarization degrees of the charge-transfer phosphorescences of the complexes and the ionization potentials of the corresponding donor molecules.

Discussion

The experimental results described in the previous section are seemingly similar to those of the fluorescence polarization experiment with TCNE complexes with benzene, toluene, *p*-xylene, and *o*-xylene studied by Prochorow *et al.*[10] They interpreted the change in the polarization relative to the charge-transfer band by means of a model of a partially disoriented complex. According to this model, the P values would decrease with a decrease in the stability of a complex (with an increase in the amount of the disoriented forms). It seems inadequate to apply this model to the phosphorescence polarization, however, since the previous experimental and theoretical studies of TCNB-methyl-substituted benzene complexes show that the lowest triplet states differ considerably from each other in electronic structure, while the lowest charge-transfer singlet states of TCNE complexes, rather, resemble each other.[3]

The transition moment between the ground state, $|G\rangle$, and the lowest triplet state, $|T\rangle$, is roughly given by[11]:

$$\mu_{TG} = \frac{\langle T|H_{so}|S_k\rangle}{|E_T - E_{S_k}|}\mu_{S_kG}$$

where $|S_k\rangle$ represents the perturbing singlet state and where E_T and E_{sk} denote the energies of $|T\rangle$ and $|S_k\rangle$ respectively. No *a priori* information about the perturbing singlet state is available. The lowest

triplet state of the TCNB complex is approximately expressed as[3]:

$$|T\rangle = \alpha|^3CT\rangle + \beta|^3DA^*\rangle$$

where $|^3CT\rangle$ and $|^3DA^*\rangle$ represent the lowest charge-transfer triplet configuration and the lowest excited triplet configuration respectively, and where $|\alpha|^2+|\beta|^2=1$. For example, $|\alpha|^2$ equals 0.95 for the TCNB-HMB complex and $|\alpha|^2$ equals 0.07 for the TCNB-benzene complex.[3]

Let us extend this relation to such an extreme case as $|\alpha|^2=0$, so that the phosphorescence of an acceptor itself can be discussed along the same lines as that of its complex compound, since the position of the phosphorescence shifts towards shorter wavelengths as the donor changes from HMB to benzene, and since the phosphorescence spectrum of TCNB itself is located at a little higher energy than that of the TCNB-benzene complex. Therefore, it may be expected that the polarization of the phosphorescence derived from the locally-excited configuration is analogous to that of TCNB itself.

Along these lines, the polarization degree of the shortest wavelength band, presumably including the 0–0 band of the phosphorescence spectrum of TCNB relative to the first and second absorption bands, was measured; negative values were obtained for both bands. This indicates that the phosphorescence of TCNB is predominantly polarized perpendicular to the molecular plane. The transition borrows its intensity from the $(\sigma\pi^*)$ transition, as in the case of aromatic hydrocarbon.[11] It then follows that $|^3DA^*\rangle$ couples with $\pi\sigma^*$ or $\sigma\pi^*$ state of TCNB through spin-orbit interaction and that the transition between $|G\rangle$ and $|^3DA^*\rangle$ is polarized alomst normal to the molecular plane.

It is easily derived, as is illustrated schematically in Fig. 10, that $|^3CT\rangle$ couples with a higher charge-transfer transition from a π donor-orbital to a σ acceptor-orbital in a way similar to that in which $|^3DA^*\rangle$ couples with the $\pi\sigma^*$ transition in the acceptor as far as one-electron spin-orbit Hamiltonian is concerned. Such a higher charge-transfer transition should also be polarized along the direction connecting the donor with the acceptor nearly perpendicular to the molecular plane. If the other terms can be neglected, the polarization of the phosphorescence can be expressed as a linear combination of the polarizations of the locally-excited transition and the charge-transfer transition described above. It may, therefore, be safely concluded that the phosphorescence is polarized nearly perpendicular to the molecular plane, irrespective of the complex. The validity of this conclusion seems to be verified by the fact that the polarization degree of the TCNB-HMB complex, in which the contribution of $|^3CT\rangle$ to $|T\rangle$ is very large, is about 0.4 relative to excitation into the charge-transfer absorption band, which is polarized nearly normal to the molecular plane.

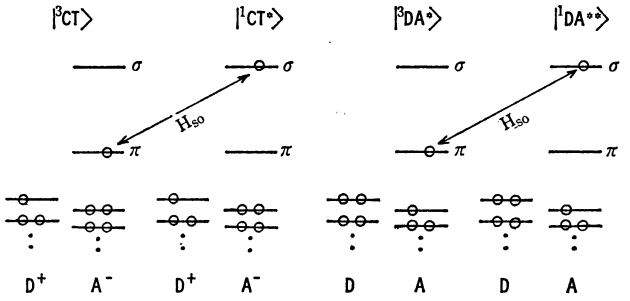

Fig. 10. Schematic diagram of one-electron spin-orbit interaction in donor-acceptor system.

It then follows that the experimental change in the values of the TCNB complexes can be determined not by the change in the phosphorescence polarization, but by the change in the transition moment of the charge-transfer absorption band. The wavefunctions of the TCNB complex in the ground and excited states are generally given by:[13]

$$\Psi_G = a^0\Phi_G + \sum b_i^0\Phi_i(D^+A^-) + \sum c_i^0\Phi_i(DA^*)$$
$$\Psi_E = a\Phi_G + \sum b_i\Phi_i(D^+A^-) + \sum c_i\Phi_i(DA^*)$$

where Ψ_G and Ψ_E represent the ground and excited state wavefunctions respectively. The transition moment is approximately expressed as:

$$\langle\Psi_G|\mu|\Psi_E\rangle \simeq \sum b_i^0 b_i\langle\Phi_i(D^+A^-)|\mu|\Phi_i(D^+A^-)\rangle + \sum (a^0c_i+c_i^0a)\langle\Phi_i(DA^*)|\mu|\Phi(DA)\rangle + \sum (a^0b_i+b_i^0a)\langle\Phi_i(D^+A^-)|\mu|\Phi(DA)\rangle.$$

In the case of TCNB complexes, $|a^0|\gg\sum|b_i^0|$, $\sum|c_i^0|$, and $|a|\ll 1$. For the sake of simplicity, we assume that $a^0=1$, $b_i^0=c_i^0=0$, and $a=0$ and that the lowest charge-transfer state mainly consists of the lowest charge-transfer singlet configuration, $\Phi(D^+A^-)$, and the lowest locally-excited singlet configuration, $\Phi(DA^*)$. The transition moment of the charge-transfer absorption band is approximately given by:

$$\mu_{S_1G} = a\mu_{CT} + b\mu_{DA^*} \quad (1)$$

where:

$$\mu_{CT} \equiv \langle\Phi(D^+A^-)|\mu|\phi(DA)\rangle$$
$$\mu_{DA}{}^* \equiv \langle\Phi(DA^*)|\mu|\Phi(DA)\rangle$$
$$a\equiv b_1 \quad \text{and} \quad b\equiv c_1.$$

The polarization of μ_{CT} is nearly normal to the molecular plane, while that of μ_{DA^*} is parallel to it. As the donor changes from benzene to HMB, the charge-transfer singlet configuration increases its contribution and the in-plane character of the direction of the transition moment decreases, but the out-of-plane character increases. The above considerations may similarly be applied to the *o*-DCNB, *m*-DCNB, and *p*-DCNB com-

Table 2. Coefficients and contribution of charge-transfer character in the lowest charge-transfer singlet state of TCNB complexes calculated from degree of polarization.

Donor	*a*	*b*	CT(%)
HMB	0.94	0.35	88
Durene	0.89	0.46	79
Mesitylene	0.75	0.66	56
p-Xylene	0.72	0.70	52
Benzene	0.67	0.74	45

Table 3. Coefficient of charge-transfer singlet configuration in the lowest charge-transfer singlet state calculated from degree of polarization.

	TCNB	*o*-DCNB	*m*-DCNB	*p*-DCNB	TCPA	PA
HMB	0.94	0.85	0.80	0.77	0.74	0.85
Durene	0.89	0.71	0.69	0.68	0.72	0.67
Mesitylene	0.75	0.54	0.54	0.55	0.62	0.62
p-Xylene	0.72				0.62	
Benzene	0.67					

plexes and may also be applied to the TCPA and PA complexes.

The a and b coefficients can be estimated from Equation (1) using the P values. By the use of the values, $|\mu_{CT}| \approx 0.3$ Å and $|\mu_{DA^*}| \approx 0.3$ Å, obtained from the experimental values of the oscillator strengths, 0.02 and 0.03 respectively, and assuming that the transition moments, μ_{CT} and μ_{TG}, are polarized normal to the molecular plane and that the μ_{DA^*} moment is polarized in the molecular plane, one can make a rough estimation of the a and b coefficients and the charge-transfer character in the lowest charge-transfer singlet state of the TCNB complexes. Table 2 summarizes the results. It can be said that these results coincide considerably well with those reported by Iwata *et al.*[12] Table 3 shows the contributions of the charge-transfer character in the lowest charge-transfer singlet states of the complexes calculated under an assumption of the same values of the transition moments as those of the TCNB complexes and using the same assumptions described above.

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