Electronic Excited States of the Intramolecular Exciplex and Charge-transfer Complex in (9,10-Dicyanoanthracene)-$(CH_2)_3$-(Naphthalene)

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In the previous paper two kinds of fluorescences due to the intramolecular exciplex (above ~200 K) and the charge-transfer complex (below ~160 K) were reported in a nonpolar solution of the (9,10-dicyanoanthracene)-$(CH_2)_3$-(naphthalene) systems. The fluorescence quantum yields as well as the fluorescence lifetimes of the exciplex and CT complex determined at several temperatures show a discontinuous change from room temperature to 77 K. The radiative and nonradiative decay constants of these fluorescent states suggest that the radiative decay in the exciplex is comparable with the nonradiative decay, while the nonradiative process is predominant in the excited state of the CT complex.

The binding energy of the exciplex has been attributed to the charge-transfer (CT) interaction between the electron donor and acceptor.[1] The CT character in the exciplex has been emphasized by the determination of the $(S_n \leftarrow S_1)$ absorption spectra.[2,3] However, there has been no information available about the difference in the properties and relationship between the exciplex and the excited state of the CT complex. The present authors previously reported that the intramolecular exciplex fluorescence was observed in the (9,10-dicyanoanthracene)-$(CH_2)_3$-(naphthalene) systems in both polar and nonpolar solvents.[4] Only in the nonpolar solvent, the intramolecular CT-complex fluorescence (λ_{max} 540 nm) was observed below ~160 K in the wavelength region longer than the exciplex fluorescence (λ_{max} 500—510 nm). The fluorescence lifetimes of the exciplex and the CT complex at various temperatures were reported to be almost independent of the temperature, and different from each other. The appreciable differences in the fluorescence lifetimes and maxima between the exciplex and CT complex suggested that there were two different excited states in the potential energy surface of the electronic interaction between the electron-donor-acceptor moieties in this compound.

Therefore, in order to elucidate the properties of these fluorescent states of the intramolecular exciplex and CT complex, we determined the fluorescence quantum yields and the radiative and nonradiative rate constants of these excited states.

Experimental

The synthesis and purification of (9,10-dicyanoanthracene)-$(CH_2)_3$-(naphthalene) (abreviated as $\beta\alpha'$- and $\beta\beta'$-DCAN) and the determination of the absorption and fluorescence spectra were reported in a previous paper.[4] The fluorescence quantum yields were measured essentially in the way described by Parker and Rees,[5] where the solution of anthracene was used as the standard. In the determination of the quantum yields of the CT complex, the intensity of the absorption spectrum at a certain wavelength (an excitation light) corresponding to the CT complex at a certain temperature (~150—77 K) was obtained by the aid of an equilibrium constant which was estimated from a straight line of $\log \varepsilon/(\varepsilon_c-\varepsilon)$ against $1/T$ mentioned in the previous paper. The fluorescence lifetimes were determined by using a coaxial-type nitrogen gas laser as an exciting light source (30 kW peak intensity at 337 nm and 3 ns duration).[6]

Results and Discussion

The mechanism for the exciplex and CT-complex formations and decay processes can be expressed as follows:

$$\begin{tikzcd} D+A^* \arrow[r, shift left, "k_3"] \arrow[d, shift right, "k_1"'] \arrow[d, squiggly, shift left, "k_2"] & (DA)^* \arrow[l, shift left, "k_4"] \arrow[d, shift right, "k_5"'] \arrow[d, squiggly, shift left, "k_6"] & (DA)_c^* \arrow[d, shift right, "k_7"'] \arrow[d, squiggly, shift left, "k_8"] \\ D+A \arrow[rr, dotted] & & (DA)_c \end{tikzcd}$$

Here, D and A are the electron donor and acceptor respectively; and $(DA)^*$ and $(DA)_C{}^*$ are the exciplex and an excited state of the CT complex respectively. The CT complex in the ground state is expressed by $(DA)_C$.

Birks *et al.* made an extensive study of the rise and decay kinetics of the pyrene excimer and determined the rate constants.[7] Recently, Yoshihara *et al.* determined the rate constants of the exciplex formation and of the decay process in the exciplex of the pyrene–*N*,*N*-dimethylaniline system.[8] They obtained the rate constant of k_3 from the concentration dependence of the intermolecular exciplex, and also evaluated k_4 and (k_5+k_6) from an analysis of the time-dependent exciplex concentration. The value of k_4 in the literature are negligible compared with those of k_3.[1,7-9] However, no determination of the k_4 in the intramolecular exciplex has ever been reported. In this paper, it is noteworthy that the intramolecular exciplex formation is independent of the concentration. Furthermore, no rise-time of the exciplex fluorescence from which k_4 might be evaluated was observed. Therefore, k_4 was assumed to be negligible compared with k_3 in this stage, and also subsequent attempts were made to study the intramolecular exciplex formation and decay process.

The fluorescence quantum yields and lifetimes of 9,10-dicyanoanthracene as determined in several solvents are shown in Table 1. Table 1 suggests that the nonradiative rate constant, k_2, in a nonpolar solvent

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Table 1. Fluorescence lifetimes and quantum yields of 9,10-dicyanoanthracene in various solvents

Solvent	τ (ns)	ϕ
MP	15.2	0.9
2-Methyl THF	15.8	0.52
Acetone	18.0	0.19
Acetonitrile	19.5	0.21

such as MP may be negligible compared with k_1. This assumption is not valid in a polar solvent, though, since the quantum yield shows a remarkable decrease in the polar solvent. In DCAN, the fluorescence quantum yield and lifetime of the 9,10-dicyanoanthracene moiety are expressed as follows:

$$\phi' = k_1(k_1+k_2+k_3)^{-1} \text{ and } \tau' = (k_1+k_2+k_3)^{-1}.$$

The results obtained here at 300 K are summarized in Table 2. If k_2 was neglected in an MP solution of DCAN, as mentioned above, the rate constant of the intramolecular exciplex formation, k_3, was directly estimated to be $1.1\times10^8\,\mathrm{s}^{-1}$ for $\beta\alpha'$-DCAN and $1.2\times10^8\,\mathrm{s}^{-1}$ for $\beta\beta'$-DCAN at this temperature from ϕ' and τ' respectively, both shown in Table 2. The value of k_3 can not be compared with those of the rate constants of the intermolecular exciplex formations in the literature,[8-10] because the former obeys different kinetics from those of the latter. Furthermore, the rate constants, k_3, at several temperatures were evaluated from the value of k_3 at 300 K and from the activation energy of the exciplex formation reported in previous papers,[4,11] where we assumed that there was no change in the entropy factor in this temperature region.

Table 2. Fluorescence lifetimes and quantum yields of DCAN's in MP

DCAN	DCA moiety[a]		Exciplex[a]		CT-Complex[d]	
	τ'(ns)	ϕ'	τ_e(ns)	ϕ_e[c]	τ_c(ns)	ϕ_c
$\beta\alpha'$-	8.0	0.097	63	0.25	127	0.13
$\beta\beta'$-	8.0	0.069	40.8	0.20	150	0.11

a) Determined at 300 K. b) Determined at 77 K.
c) Apparent quantum yields mentioned in the text.

The apparent fluorescence quantum yield of the exciplex, ϕ_e, can be expressed by the following equation:[8]

$$\phi_e = \phi_e' \frac{k_3\tau}{1+k_4\cdot\tau_e'}\left\{1+\frac{k_3\tau}{1+k_4\cdot\tau_e'}\right\}^{-1} = \phi_e'\cdot f.$$

Here, $\tau=(k_1+k_2)^{-1}$, $\tau_e'=(k_5+k_6)^{-1}$ and $\phi_e'=k_5\cdot\tau_e'$. Since k_4 was neglected, as has been mentioned above, f, k_5 and k_6 can be estimated by the aid of the τ, τ_e', k_3 and ϕ_e obtained in an MP solution of DCAN. These results, as determined at 300 K, are summarized in Table 3. These quantum yields, and the radiative and nonradiative rate constants of the exciplex at several temperatures, were determined in an MP solution of $\beta\beta'$-DCAN; the results are shown in Fig. 1.

On the other hand, the fluorescence quantum yields of the CT complex in an MP solution of $\beta\beta'$-DCAN at several temperatures below ~150 K were determined by the method described in the experimental section.

Table 3. Radiative and nonradiative rate constants (in units of s^{-1}), and fluorescence quantum yields in DCAN's (in MP)

DCAN	DCA moiety[a]			Exciplex[a]		CT-complex	
	k_1 $\times10^{-7}$	k_2+k_3 $\times10^{-8}$	ϕ'_e[c]	$k_5\times$ 10^{-6}	$k_6\times$ 10^{-6}	$k_7\times$ 10^{-6}	$k_8\times$ 10^{-6}
$\beta\alpha'$-	1.2	1.13	0.54	8.3	7.5	1.05	6.8
$\beta\beta'$-	0.86	1.2	0.42	10.4	14	0.7	5.9

a) Results evaluated from the data at 300 K.
b) Results evaluated from the data at 77 K.
c) Estimated quantum yields of the exciplex mentioned in the text.

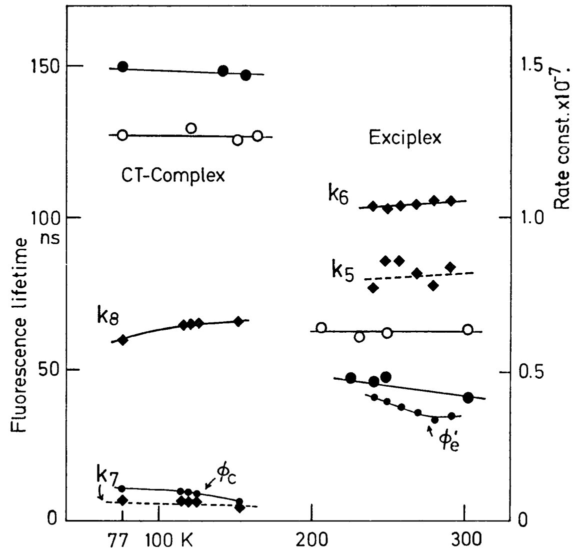

Fig. 1. Temperature dependence of the fluorescence lifetimes determined at 560 nm, —○—○— and —●—●— are $\beta\alpha'$-, and $\beta\beta'$-DCAN, respectively, and of the fluorescence quantum yields, and the radiative and nonradiative rate constants of the exciplex and the CT-complex in an MP solution. Concentrations are approximately 10^{-6}M. An unit of an ordinate for the decay rate constants is $10^7\mathrm{s}^{-1}$.

These results and the decay rate constants of the CT complex of $\beta\beta'$-DCAN at several temperatures are shown in Fig. 1. These quantum yields and the rate constants of the exciplex and the CT complex are both almost temperature-independent. It is unlikely that the quantum yield and also the rate constant can continuously change from the exciplex to the CT complex in the temperature region of ~200—160 K, as is shown in Fig. 1, where the fluorescence in the 500—550 nm region was almost quenched and was indistinguishable between the exciplex and the CT complex. This is because the solvent (MP) used here shows no steep change in viscosity in this temperature region.

Recently it has been suggested that the fluorescent state of the exciplex is identical with that of the corresponding CT complex, though no comparison of the exciplex fluorescence with that of the CT complex was made in the same electron-donor-acceptor system. Very recently, Itoh and Mimura reported experimental evidence for an identical fluorescent state of the inter-

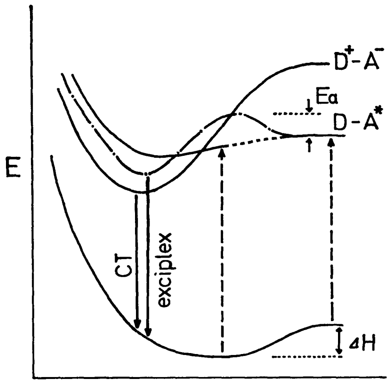

Fig. 2. The potential energy curves of the exciplex and the CT-complex.

molecular exciplex and CT complex in the 9,10-dicyanoanthracene–2-methylnaphthalene system.[12] The experimental behaviors of the intramolecular exciplex and CT complex reported here and also in the previous paper[4] demonstrate that these two fluorescences are from individual fluorescent states, as is illustrated in Fig. 2. Mataga *et al.*[13] reported the radiative and nonradiative rate constants in the exciplex of the pyrene–*N*,*N*-dimethylaniline system in the nonpolar solvent to be 2.4×10^6 s^{-1} and 2.6×10^6 s^{-1} respectively. Kobayashi *et al.*[14] made an extensive study of the CT complex of tetracyanobenzene and reported the radiative and nonradiative rate constants of the CT complex in a nonpolar solvent to be 10^{4-5} s^{-1} and 10^{6-7} s^{-1} respectively. As is shown in Fig. 1 and in Table 3, the radiative and nonradiative rate constants in the exciplex are comparable to each other, while the latter seems to be the main process in the CT complex. The decay constants from room temperature to 77 K obtained here are further confirmation of our arguments that the fluorescence above ~200 K is to be ascribed to the exciplex, and those below ~160 K, to the CT complex, and that there are two different fluorescent states in the intramolecular electronic interaction between the electron donor and acceptor moieties. These electronic interactions leading to the difference in the excited fluorescent states of the exciplex and the CT complex can be understood by the argument that the internal or geometrical conversion from their respective Franck-Condon excited states to the identical fluorescent state, which may be allowed in the intermolecular interaction,[12] is forbidden in these chain compounds by the steric factor concerned with the trimethylene chain.

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