On the Solvent-Induced Changes of Electronic Structures of Intramolecular Exciplexes

Shinzaburo Masaki, Tadashi Okada, Noboru Mataga,*
Yoshiteru Sakata,** and Soichi Misumi**
The Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560
***The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565*

(Received September 16, 1975)

Effects of solvent polarity upon the electron donor-acceptor interactions in the excited state of *p*-$(CH_3)_2N\,C_6H_4$-$(CH_2)_n$-(9-anthryl) (n=0, 1, 2, 3) and *p*-$(CH_3)_2NC_6H_4$-$(CH_2)_n$-(1-pyrenyl) (n=1, 2, 3) have been investigated by means of fluorescence spectral measurements and theoretical calculations based on some simplified models. The solvent-induced electronic structural changes during the excited state lifetime have been demonstrated for some of the above intramolecular exciplexes.

The nature of the CT (charge transfer) interaction in the excited electronic state is a subject under the most lively investigation at present. For example, it is well-known that many aromatic molecules in solution form exciplexes in the singlet excited state.[1)] Detailed studies on the structures and dynamic behaviors of exciplex systems are now being made, mainly by means of time-resolved fluorescence measurements as well as transient absorption spectral measurements by the laser photolysis method. On the other hand, similar studies have been made on the excited state of CT complexes (which are stable in the ground state), such as the TCNB(1,2,4,5-tetracyanobenzene)-aromatic hydrocarbon complexes.[2—6)] Owing to these investigations, the nature of the CT interactions in the excited electronic state has been elucidated to a considerable extent and the results of these investigations appear to be important from the viewpoint of the photochemical reaction mechanisms in solution.

Upon increasing the solvent polarity, both the fluorescence quantum yield and the decay time of some typical heteroexcimers, such as pyrene-DMA (*N,N*-dimethylaniline) and anthracene-DEA (*N,N*-diethylaniline), decrease, and the fluorescence yield decreases more rapidly with increasing solvent polarity than does the corresponding fluorescence lifetime.[7,8)] There are two alternative interpretations of these observations.

(a) Solvent-induced Change of Electronic and Geometrical Structure of the Exciplex.[7)] The exciplex state may be considered as a resonance hybrid of the electron transfer configuration (A^-D^+) mixed with the locally excited configuration (A^*D) or (AD^*). The solvation of the exciplex by the polar solvents will oppose the electronic delocalization between A and D since the solvation energy increases with increasing charge separation in the exciplex, *i.e.*, with its increasing dipole moment. This is true whether the solvation can be approximated by the interaction of a solute dipole with the surrounding dielectric continuum[9)] or it is described by the $1:n$ electrostatic complex formation with the polar solvent molecules.[10,11)] Furthermore, the strong solvation may induce the change of geometrical structure of the exciplex leading to the decrease of the electronic delocalization interaction between A and D. Thus, the exciplex electronic structure may become more polar with increasing polarity of the solvent and this change of the electronic structure would lead to the decrease of the radiative transition probability. The radiationless transition probability, however, increases with solvent polarity because the energy gap between the relevant electronic levels becomes smaller in a more polar solvent and, furthermore, because of the ionic dissociation of the complex in a more or less polar solvent.

(b) Competition between the Ionic Dissociation and the Fluorescent Exciplex Formation in the Encounter Complex.[8)]

$$\begin{tikzcd}
 & & (A^-D^+)^* \arrow[dd, "k_i"] & \\
A^* + D \arrow[r] & A^*\cdots D \arrow[ur, "k_c"] \arrow[dr, "k_{ip}"'] & & \\
 & & (A_s^-\cdots D_s^+) \arrow[r, "k_d"] & A_s^- + D_s^+
\end{tikzcd}$$

where $(A^-D^+)^*$ is the fluorescent exciplex and $(A_s^-\cdots D_s^+)$ represents a solvated ion-pair which is nonfluorescent. Almost complete charge transfer between D and A in the exciplex is assumed here, while partial charge transfer is postulated in the case of (a). It is assumed that k_{ip} and k_i are increased in polar solvents while k_c is almost independent of the solvent polarity and, moreover, the electronic structure of the complex may be independent of the solvent polarity.

According to the recent laser photolysis studies,[12)] the solvent-induced electronic structural change does not seem to be very important for the interpretation of the effect of solvent polarity upon the fluorescence yield and decay time of such strongly polar exciplexes as pyrene-DMA and anthracene-DEA systems. However, the phenomenon of the solvent-induced electronic structural change may exist in principle and seems to be of some importance in general for the interpretation of electronic structures of molecular complexes in solution, since they have more flexible structures than the ordinary molecules. The observation by Schneider and Lippert[13)] that the fluorescence spectra of 9,9′-bianthryl depends considerably on the solvent polarity, showing a red shift as the polarity is increased, seems to be a special case of a competition between the delocalization tendency and the solvation as described in (a). Namely, in the case of 9,9′-bianthryl, which consists of two weakly interacting identical moieties, there arise energy minima corresponding to solvated polar (unsymmetrical) states which are more stable than the nonpolar symmetrical ones at sufficiently high solvent polarities.[14)]

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* To whom all correspondence should be addressed.

Recently, we have examined the solvent effect upon the $S_n \leftarrow S_1$ spectra of this compound by using the mode-locked ruby laser.[15] Although the $S_n \leftarrow S_1$ spectra in hexane are not the same as those of anthracene, they are somewhat similar to each other. The spectra observed in acetone are quite different from those in hexane and rather similar to those of anthracene ions.[15] This is a direct demonstration of the solvent-induced electronic structural change. This result of a remarkable solvent effect on the $S_n \leftarrow S_1$ spectra is similar to the case of the solvent effect upon the $S_n \leftarrow S_1$ spectra of 9-(4-dimethylaminophenyl)anthracene which we have observed previously.[16]

Now, in order to elucidate the electronic structures and the mechanisms of the dynamical behaviors of exciplex systems, we have been making detailed studies of the following intramolecular exciplex systems: p-$(CH_3)_2N\ C_6H_4$-$(CH_2)_n$-(9-anthryl) (n=0, 1, 2, 3, abbreviated as A_0, A_1, A_2, A_3, respectively) and p-$(CH_3)_2N\ C_6H_4$-$(CH_2)_n$-(1-pyrenyl) (n=1, 2, 3, abbreviated as P_1, P_2, P_3, respectively). The solvent shifts of the fluorescence bands of these intramolecular exciplexes have been measured and analyzed by a theoretical method which is an extension of the previous ones,[17,18] and the solvent-induced electronic structural change has been demonstrated.

In the following the results of these investigations will be described from the viewpoint of the solvent-induced electronic structural change of the composite molecular systems and of the geometrical restrictions on the exciplex formation.

Experimental

Synthesis of the compounds, A_0, A_1, A_2, A_3, P_1, P_2, and P_3, will be reported in a separate paper.[19]

The following solvents were used for the measurements. (The numbers in parentheses are those attached to the observed points in the figures.) Hexane (3), methylcyclohexane (4), cyclohexane (5), dibutyl ether (9), diethyl ether (13), chloroform (14), isobutyl acetate (17), ethyl acetate (18), methyl acetate (19), tetrahydrofuran (20), dichloromethane (21), pyridine (23), isopentyl alcohol (25), 1-butanol (26), 1-propanol (28), acetone (29), and acetonitrile (31), were spectrograde reagents and used without purification. Isopentane (1), pentane (2), decalin (6), tetralin (7), diisopentyl ether (8), dipropyl ether (10), acetal (11), diisopropyl ether (12), 1-hexanol (24), isobutyl alcohol (27), and ethanol (30), were purified by the standard method.[20] Butylacetate (15), ethyl butyrate (16), 1,1,2,2-tetrachloroethane (22), were G. R. grade reagents and used without purification.

Fluorescence spectra were measured by an Aminco-Bowman or a Hitachi MPF-2A spectro-photofluorometer. Solutions were deaerated by means of the freeze-pump-thaw cycles or flushed with nitrogen. For the measurements at low temperatures, a cuvette was immersed in ethanol in a quartz Dewar vessel and the temperature of ethanol was controlled by dropping liquid nitrogen. For the measurements at higher temperatures than room temperature, the cuvette was immersed in hot water in the quartz Dewar.

Results and Discussion

Solvent Effects upon Fluorescence Spectra. Absorption spectra of A_1, A_2, A_3, P_1, P_2, and P_3 do not show any indication of the ground state interaction. However, the absorption spectra of A_0 are a little broadened compared with those of anthracene, indicating a weak ground state interaction between the two moieties. The longest wavelength absorption band of A_0 may be a superposition of the anthracene band slightly modified by the substitution and a very weak CT band.[16,21] Although the absorption spectra of these systems show little dependence on the solvent polarity, the latter affects considerably their fluorescence spectra. For instance, the fluorescence spectra of A_2 and P_1 show remarkable solvent dependence, as indicated in Fig. 1. Quite similar results have been obtained for A_1.

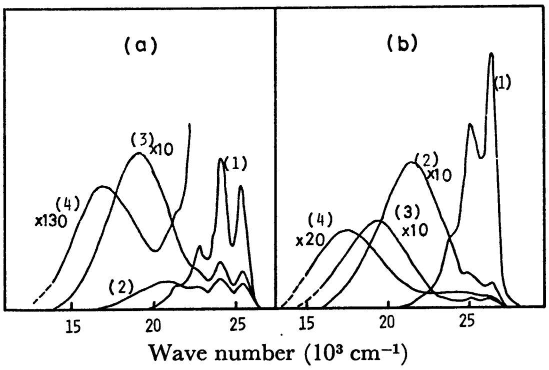

Fig. 1. Fluorescence quantum spectra of A_2 (a) and P_1 (b) in various solvents.
Solvents: 1. hexane, 2. diethyl ether, 3. isobutyl acetate, 4. isobutyl alcohol.

The fluorescence spectra of A_1, A_2, and P_1 in nonpolar solvent can be ascribed to the anthracene or pyrene part (LE (local excited state) fluorescence). In polar solvents, they show the exciplex fluorescence band in addition to the LE fluorescence band. The exciplex band shows a remarkable red shift with increase of the solvent polarity, while the wave number of the LE band does not depend on the solvent polarity. Thus, A_1, A_2 and P_1 show dual fluorescence spectra in polar solvents, but not in nonpolar solvents.

The fluorescence spectra of P_2 and P_3 in various solvents are indicated in Fig. 2. The results for A_3

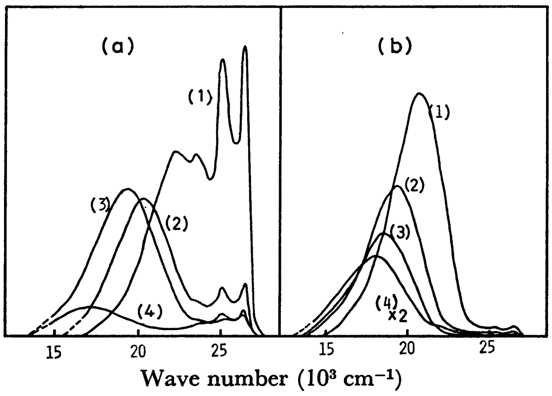

Fig. 2. Fluorescence quantum spectra of P_2 (a) and P_3 (b) in various solvents.
Solvents: 1. hexane, 2. diethyl ether, 3. butyl acetate, 4. isobutyl alcohol.

are rather similar to those in Fig. 2. In the case of these systems, both the exciplex fluorescence and the LE fluorescence bands can be observed even in nonpolar solvents, although the exciplex fluorescence yield of P_3 in a nonpolar solvent is much larger than that of P_2.

The above results for P_2 and A_2 suggest that the geometrical structure of P_2 is more favorable for the exciplex formation than that of A_2, since the electron affinity of pyrene is almost equal to or a little smaller than that of anthracene.

In contrast to the fluorescence spectra of $A_n(n=1,2,3)$ and $P_n(n=1,2,3)$, A_0 exhibits a single fluorescence band and shows a continuous red shift with increase of the solvent polarity.[16)]

We have plotted the energy of the fluorescence ($h\nu_f$) of these compounds against the polarity parameter $f(\varepsilon,n)=(2(\varepsilon-1/2\varepsilon+1)-(n^2-1/2n^2+1))$, where ε and n are the dielectric constant and the refractive index of the solvent, respectively. Of course, the solute-solvent interaction may be a more or less specific molecular interaction, so that the points in the figures are rather scattered around the average values.

The plot for A_0 cannot be represented by one straight line; it is curved or represented by a superposition of several lines of different slopes.[16)] This result indicates the solvent-induced change of excited electronic structure. The change of the electronic structure in the case of A_0 can be concluded also from the solvent dependence of the fluorescence yield and lifetime as well as the solvent effect on the $S_n \leftarrow S_1$ absorption spectra.[16,21)]

In the case of A_1, A_2, and P_1, the CT fluorescence appears at the values of the polarity parameter $f(\varepsilon,n)\approx 0.3$—$0.4$, where its red shift with the solvent polarity is especially large. Compared with the case of sandwich type exciplexes, the stabilization of the CT state due to the Coulomb force between the pair may be smaller in these cases owing to the larger separation between

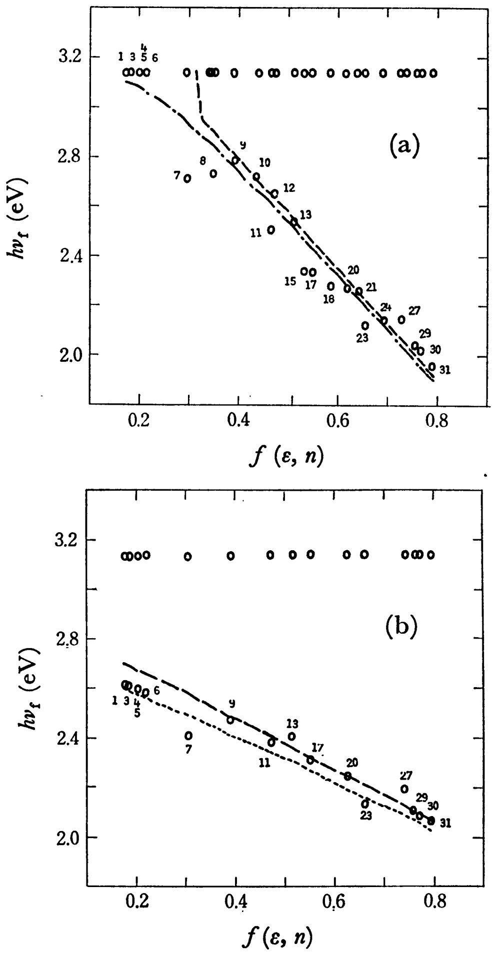

Fig. 3. Comparison between the observed and the calculated $h\nu_f$ values of A_1 (a) and A_3 (b).
o: observed value.
Calculated curves.
a. ———: α=0.05 eV, ————: α=0.3 eV.
b. ———: α=0.0 eV, --------: α=0.3 eV.

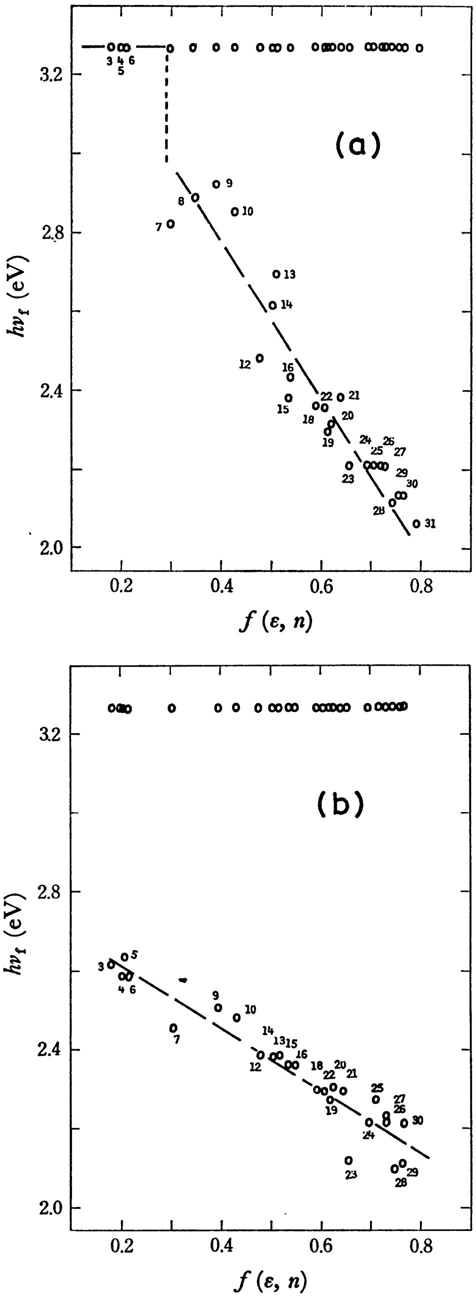

Fig. 4. Observed $h\nu_f$ vs. $f(\varepsilon, n)$ relations for P_1 (a) and P_3 (b).

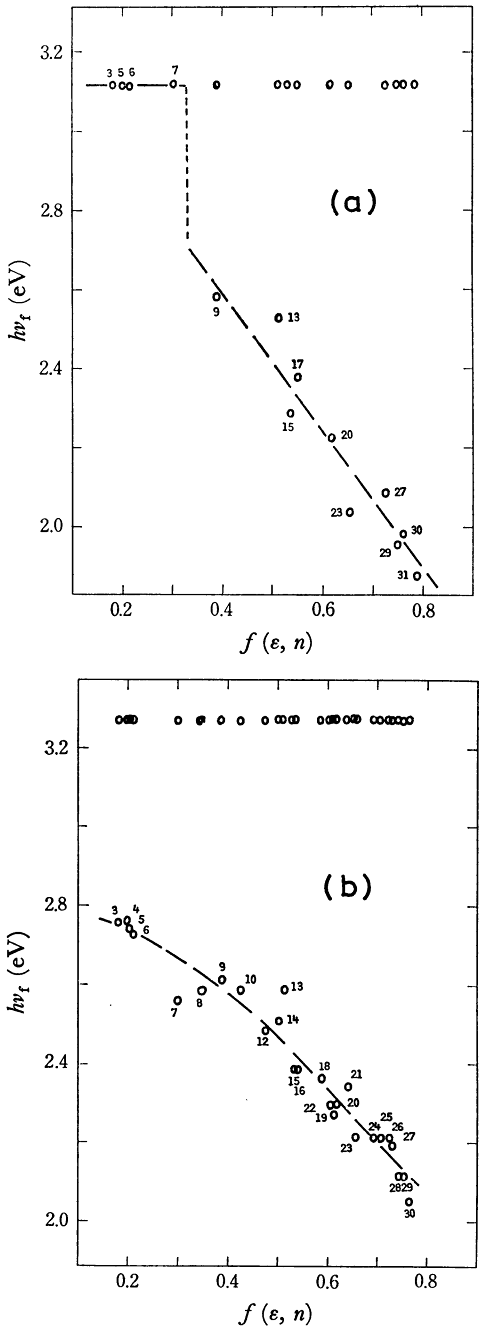

Fig. 5. Observed $h\nu_f$ *vs.* f (ε, n) relations for A_2 (a) and P_2 (b).

the two moieties. Therefore, the electron transfer state is placed at higher energy than the LE state (S_1) of anthracene or pyrene and there may arise only a very weak interaction between the electron transfer configuration and the LE configuration because of the long distance between the two groups and the unfavorable geometrical configuration for the delocalization interaction. However, because their dipole moments in the CT state are much larger than those of the sandwich type exciplexes, the CT state may be stabilized rather strongly by the interaction with the polar solvent.

The energy of the CT state in solution may be given by Eq. 1, if we neglect the delocalization interaction between the two moieties.

$$\begin{aligned} E_{CT} &= I - A - C - H_s \\ &= I - A - C - (\mu_e^{eq^2}/a^3)(\varepsilon - 1/2\varepsilon + 1) \\ &= I - A - C - \frac{1}{2}\mu_e^{eq^2}f_\varepsilon \qquad (1) \end{aligned}$$

where I and A are the ionization potential of the donor and electron affinity of the acceptor, respectively, C is the coulomb interaction energy between the donor cation and acceptor anion calculated by using the Hückel MO's putting point charges at each AO, and H_S is the solvation energy of the ion-pair. We have approximated here H_S by the interaction energy of a dipole with the surrounding dielectric continuum according to Onsager's reaction field theory. a is the cavity radius in the reaction field theory and μ_e^{eq} is the dipole moment of the excited equilibrium state. For example, the value of $(\mu_e^{eq^2}/a^3)$ for S_1 was estimated to be 2.1 eV from the slope of the $h\nu_f$—$f(\varepsilon,n)$ linear relation in Fig. 3. Taking I=7.5 eV, A=0.5 eV, C=3.2 eV, and $(\varepsilon-1/2\varepsilon+1)\approx0.26$ (the CT fluorescence appears above the value of $(\varepsilon-1/2\varepsilon+1)\approx0.26$), E_{CT} was estimated to be 3.25 eV. (For the evaluation of C, it was assumed that the long axis of anthracene is parallel with the short axis of DMA and the angle between the short axis of anthracene and the long axis of DMA is 109°28′.) Since the ground state will have no dipole moment due to CT from DMA to anthracene, the Franck-Condon (FC) ground state may be destabilized with respect to solvation. Again by using the dielectric continuum approximation, the destabilization energy amounts to

$$\begin{aligned} \delta E_g^{FC} &= (\mu_e^{eq^2}/a^3)[(\varepsilon - 1/2\varepsilon+1) - (n^2 - 1/2n^2 + 1)] \\ &= (1/2)\mu_e^{eq^2}(f_\varepsilon - f_n) \qquad (2) \end{aligned}$$

$\delta E_g^{FC}\approx0.12$ eV at $(\varepsilon-1/2\varepsilon+1)\approx0.26$ since $(n^2-1/2n^2+1)\approx0.2$ for almost all solvents used in the present work. Therefore, $h\nu_f=E_{CT}-\delta E_g^{FC}=3.13$ eV. This $h\nu_f$ value is almost equal to that of anthracene LE fluorescence. The circumstance in the case of A_2 and P_1 seems to be quite analogous. Therefore, the solvent-induced change of the electronic structure of these compounds may be regarded as a solvent-induced reversal of two energy levels which do not interact with each other or do interact only very weakly. In other words, the solvent-induced changes of the fluorescence spectra of these compounds can be interpreted satisfactorily on the basis of the solvation of the CT state calculated with the dielectric continuum theory. However, as was pointed out in the introductory part, it may be possible that the solvation of the CT state is accompanied by some change of the geometrical structure. For example, the molecular plane of anthracene or pyrene might be perpendicular to that of DMA in the CT fluorescent state, so that the electronic delocalization interaction between the two moieties would become negligibly small.

The change of the excited electronic structure of these molecules induced by solvation can be observed also by changing the temperature of the solution, as indicated in Fig. 6 for the case of A_1 in dibutyl ether. At high temperatures, one can observe only the anthracene LE fluorescence. When the temperature is lowered,

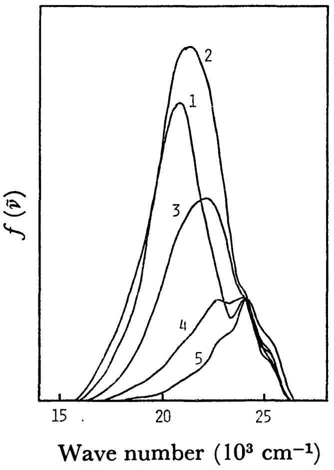

Fig. 6. Temperature effect on the fluorescence of A_1 in *n*-butylether. The spectra are normalized at the peak of anthracence LE fluorescence (24.2×10^3 cm^{-1}). Temperature (°C): (1) −61.5, (2) −25.3, (3) −3.5, (4) 26.5, (5) 78.5.

the exciplex fluorescence band appears, becomes stronger, and shifts to red. At sufficiently low temperatures, the LE band is again a little strengthened in addition to the further red shift of the exciplex band. At high temperatures, the CT state will not be stabilized sufficiently for the exciplex band to appear because of the weak solvation. There seems to be a competition between the LE fluorescence and the change of the excited electronic structure due to solvation. At sufficiently low temperatures, the solvation process as well as the accompanying structural changes may become slow because of the high viscosity, leading to a strengthening of the LE band.

The plot of the energy of the exciplex fluorescence against the solvent polarity parameter $f(\varepsilon, n)$ in the case of P_3 and A_3 can be represented approximately by an almost straight line. Therefore, only small solvent-induced electronic structural changes seem to arise in the case of these exciplexes and their electronic structures may be considerably polar even in a nonpolar solvent, since their CT states are presumably lower than the LE state even in nonpolar solvents due to the strong Coulomb interaction between the two moieties. The situation in the case of P_2 seems to be analogous. However, the plot of $h\nu_f$ against $f(\varepsilon, n)$ appears a little curved, indicating a small change of the electronic and, presumably, geometrical structures of the exciplex fluorescent state induced by the interaction with polar solvent molecules.

Remarks on the Mechanism of Charge Transfer Process in the Intramolecular Exciplex Systems. At any rate, the CT fluorescence state should be formed from the LE state owing to the solvation as well as the change of the geometrical structure, as indicated in Eq. 3.

$$\begin{tikzcd}
\text{LE flourescence} & \text{exciplex fluorescence} \\
(\text{LE}) \arrow[u] \arrow[d] \arrow[r, "\text{change of structure}", "\text{solvation}"'] & (\text{CT}) \arrow[u] \arrow[d] \\
\text{quenching} & \text{quenching}
\end{tikzcd} \qquad (3)$$

For example, the fluctuation of the relative orientations of two aromatic rings into the configuration most suitable for the charge transfer will occur frequently in the case of A_1 and P_1. The charge transfer from the *N,N*-dimethylaniline group to an anthracene or pyrene nucleus might be induced by this orientational fluctuation as well as those of polar solvent molecules, and the generated CT state may be stabilized by the orientational relaxation of solvents, *i.e.*, by the solvation process.

The change of structure seems to be especially important for A_2 and P_2 as well as A_3 and P_3 to form the exciplex fluorescent state. In the case of A_2 and P_2, their structures in the ground and the excited FC state are presumably *trans* or *gauche* form with respect to the CH_2–CH_2 single bond. They will change partly to *cis* form where the charge transfer occurs, and will be solvated in the polar solvent, resulting in the exciplex fluorescence. As was pointed out already, the Coulomb interaction energy between the donor cation and acceptor anion in the *cis* form of P_2 seems to be larger than that of A_2, since the exciplex fluorescence of P_2 can be observed even in nonpolar solvents. The situation in the case of A_3 and P_3 seems to be analogous: namely, their ground state structure may be an extended form and the sandwich structure seems to be formed during the excited state lifetime.

Analysis of the Observed Results on the Basis of Some Theoretical Models. Now, we will try to explain the above experimental results on the basis of some theoretical models. We assume the wave function of Eq. 4 for the intramolecular exciplex systems.

$$\Psi = C_1\Psi(A^-D^+) + C_2\Psi(A^*D) + C_3\Psi(AD) \qquad (4)$$

where the 1st term represents the lowest CT configuration, the 2nd is the locally excited (^1L_a) configuration, and the last term is the ground configuration. The Hamiltonian of the system may be given by:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}' \qquad (5)$$

where $\mathscr{H}_0$ is the Hamiltonian of the exciplex in the absence of the solvent and $\mathscr{H}'$ represents the electrostatic interaction with the solvent molecules. Since the solute-solvent interaction is essentially "molecular" interaction between a solute molecule and the surrounding solvent molecules, the above treatment in terms of a dielectric continuum model may be only a rough approximation. Presumably, a more appropriate treatment is to regard the interaction of the solute with the nearest neighbor solvent molecules as a 1 : *n* electrostatic complex formation and to approximate the interactions with solvent molecules further apart using the dielectric continuum model. This is a rather old problem in the theoretical treatment of the molecular interactions in liquid solutions, but even at present a rather difficult problem.

If we regard the solute-solvent interaction as an electrostatic molecular complex formation, we must calculate the interaction energy for an individual case by using the wave function of Eq. 4 in which it is necessary to assume some specified form of $\mathscr{H}'$ for several interacting molecules. However, such a calculation is rather difficult in practice. In view of the fact that the solvent-induced changes of fluorescence spectra of A_1, A_2 and P_1 can be well interpreted by assuming the interaction of an excited solute dipole with the surrounding solvent molecules to be approximated by the dielectric continuum, we approximate here $\mathscr{H}'$ by a simple continuum model using the Onsager's reaction field. On the basis of this simplified model, we try to give an interpretation of the general features of the solvent effects on the exciplex fluorescence.

We put

$$\mathscr{H}' = -\vec{\mu}_{\text{op}}\vec{F} = -\vec{\mu}_{\text{op}}\vec{\mu}f_\varepsilon \qquad (6)$$

where $\vec{\mu}_{\text{op}}$ is the dipole operator, $\vec{F}$ is the Onsager's reaction field, and $\vec{\mu}$ is given by:

$$\begin{aligned}\vec{\mu} &= \langle\Psi|\vec{\mu}_{\text{op}}|\Psi\rangle \simeq C_1^2\langle\Psi(\text{A}^-\text{D}^+)|\vec{\mu}_{\text{op}}|\Psi(\text{A}^-\text{D}^+)\rangle \\ &= C_1^2\vec{\mu}_\text{o} \qquad (7)\end{aligned}$$

We denote the matrix elements of the Hamiltonian as follows:

$$\begin{aligned}\langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}|\Psi(\text{A}^-\text{D}^+)\rangle &= \langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}_0|\Psi(\text{A}^-\text{D}^+)\rangle \\ &\quad + \langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}'|\Psi(\text{A}^-\text{D}^+)\rangle \\ &= E_\text{c} - \langle\Psi(\text{A}^-\text{D}^+)|\vec{\mu}_{\text{op}}\vec{F}|\Psi(\text{A}^-\text{D}^+)\rangle \\ &= E_\text{c} - C_1^2\mu_\text{o}^2 f_\varepsilon \qquad (8)\end{aligned}$$

$$\left.\begin{aligned}&\langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}|\Psi(\text{A*D})\rangle \\ &\qquad \simeq \langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}_0|\Psi(\text{A*D})\rangle = \alpha \quad \text{(a)} \\ &\langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}|\Psi(\text{AD})\rangle \\ &\qquad \simeq \langle\Psi(\text{A}^-\text{D}^+)|\mathscr{H}_0|\Psi(\text{AD})\rangle = \beta \quad \text{(b)} \\ &\langle\Psi(\text{A*D})|\mathscr{H}|\Psi(\text{A*D})\rangle \\ &\qquad \simeq \langle\Psi(\text{A*D})|\mathscr{H}_0|\Psi(\text{A*D})\rangle = E_\text{e} \quad \text{(c)} \\ &\langle\Psi(\text{AD})|\mathscr{H}|\Psi(\text{AD})\rangle \\ &\qquad \simeq \langle\Psi(\text{AD})|\mathscr{H}_0|\Psi(\text{AD})\rangle = E_\text{g} \quad \text{(d)}\end{aligned}\right\} \qquad (9)$$

In terms of these matrix elements, the secular equations may be written as:

$$\begin{aligned}&C_1(E_\text{c} - C_1^2\mu_0^2 f_\varepsilon - E) + C_2\alpha + C_3\beta = 0 \\ &C_1\alpha + C_2(E_\text{e} - E) = 0 \\ &C_1\beta + C_3(E_\text{g} - E) = 0 \qquad (10)\end{aligned}$$

Thus, the wave function Ψ depends upon the solute-solvent interaction $\mathscr{H}'$, while $\mathscr{H}'$ depends on the charge distribution determined by Ψ. Therefore, one must solve the nonlinear Eq. 10. However, in the present case, the solution can be obtained by solving Eq. 11, instead of doing an iterative calculation.

$$\left\{E_\text{c} - E - \frac{\alpha^2}{E_\text{e} - E} + \frac{\beta^2}{E}\right\}\left\{1 + \frac{\alpha^2}{(E_\text{e} - E)^2} + \frac{\beta^2}{E^2}\right\} = \mu_0^2 f_\varepsilon \qquad (11)$$

In order to obtain the energies relevant to the frequency of the exciplex emission, one must add to the energy obtained from Eq. 11 the polarization energy of the solvent, $E_{\text{pol}} = (1/2)\vec{\mu}\vec{F}$. We denote the lowest and the 2nd lowest eigenvalues obtained from Eq. 11 as E_0 and E_1, respectively. Then, the energies of the excited equilibrium state (E_e^{eq}) and the FC ground state (E_g^{FC}) may be given by Eq. 12 and Eq. 13, respectively.

$$E_\text{e}^{\text{eq}} = E_1 + \frac{1}{2}\vec{\mu}_\text{e}^{\text{eq}}\vec{F}_\text{e}^{\text{eq}} = E_1 + \frac{1}{2}\mu_\text{e}^{\text{eq}^2} f_\varepsilon = E_1 + \frac{1}{2}C_1^4\mu_0^2 f_\varepsilon \qquad (12)$$

$$\begin{aligned}E_\text{g}^{\text{FC}} &= E_0 - \vec{\mu}_\text{g}^{\text{FC}}\vec{\mu}_\text{e}^{\text{eq}}(f_\varepsilon - f_n -)\mu_\text{g}^{\text{FC}^2} f_n + \frac{1}{2}\mu_\text{e}^{\text{eq}^2}(f_\varepsilon - f_n) + \frac{1}{2}\mu_\text{g}^{\text{FC}^2} f_n \\ &= E_0 - C_1'^2 C_1^2\mu_\text{o}^2(f_\varepsilon - f_n) + \frac{1}{2}C_1^4\mu_\text{o}^2(f_\varepsilon - f_n) \\ &\quad - \frac{1}{2}C_1'^4\mu_0^2 f_n \qquad (13)\end{aligned}$$

where μ_g^{FC} is the dipole moment of the FC ground state and C_1 and C_1' represent respectively the coefficients of $\Psi(\text{A}^-\text{D}^+)$ in the lowest excited and the ground state wave functions obtained by solving Eq. 10 and Eq. 11. Thus, the energy of the exciplex fluorescence may be given by

$$h\nu_\text{f} = E_1 - E_0 + \frac{1}{2}(C_1^4 + C_1'^4)\mu_\text{o}^2 f_n + C_1^2 C_1'^2\mu_0^2(f_\varepsilon - f_n) \qquad (14)$$

The solvent shift of the fluorescence of A_1, for example, can be well reproduced by means of the following parameters, as indicated in Fig. 3: $E_\text{c} = 3.70$ eV, $E_\text{e} = 3.14$ eV, $|\vec{\mu}_0| = 28.0$ D, $\alpha = 0.05$ eV, and $\beta = 0$. Since α is very small and $\beta = 0$, this case can be regarded as a solvation induced reversal of two energy levels, which is the same conclusion as already obtained by the simplified procedure. We have obtained a similar calculated result for P_1. Although we have not made any detailed calculation for A_2, the circumstances in A_2 seems to be rather similar to those in A_1.

In the case of A_0, however, we cannot neglect β, but we must use fairly large values for both α and β in order to reproduce the observed result. We have confirmed that the result of calculation using the following values of parameters: $E_\text{c} = 3.1$ eV, $|\vec{\mu}_0| = 20.1$ D, $\alpha = 0.4$ eV, and $\beta = 0.3$ eV or $\beta = 0.4$ eV, is rather close to the experimental result. The calculated value of C_1^2 shows a gradual increase with the increase of the solvent polarity, in contrast to the case of A_1 where C_1^2 shows a sudden increase at $f(\varepsilon, n) \approx 0.33$. However, recent results[21] of detailed studies upon the solvent dependence of the fluorescence yield and lifetime of A_0 indicate a rather drastic change of electronic structure when the solvent is changed from diethyl ether ($f(\varepsilon, n) = 0.512$) to isobutylacetate ($f(\varepsilon, n) = 0.548$). In order to explain this drastic structural change, we need a more sophisticated theoretical treatment. Therefore, roughly speaking, the plot of $h\nu_\text{f}$ *vs.* $f(\varepsilon, n)$ for A_0 might be represented approximately by the superposition of two lines of different slopes. Nevertheless, the solvent-induced electronic structural change of excited A_0 is different from those in the case of A_1, A_2 and P_1, in the fact that A_0 shows a single fluorescence band. The single fluorescence band of A_0 seems to be ascribed to a stronger electronic interaction between two moieties than in the case of A_1, A_2 and P_1, which is consistent with the larger values of parameters α and β.

In the case of A_3 and P_3, the solvation induced electronic structural change is not large and the electronic structure of the exciplex seems to be considerably polar even in a nonpolar solvent. Actually, in order to reproduce the observed result, it was found for A_3 that $E_\text{c} = 2.90$ eV, which is lower than the LE state, leading to the strongly polar structure of the exciplex, and $\alpha \approx 0$—0.3 eV and β can be neglected. The calculated result is compared with the experimental values in Fig. 3. The change of C_1^2 with solvent polarity was rather small. We have not made such a calculation for P_3, but the results may be very similar to the present one. Although we have not made any calculation in the case of P_2, a similar calculation with smaller values of the energy gap ($E_e - E_c$) than those for the case of $n=3$, might explain the observed results.

Concluding Remarks

We have demonstrated that the electronic structure of some molecular composite systems are liable to change remarkably by the interaction with polar solvent molecules in the excited electronic state. Although the strongly polar intermolecular exciplex systems undergo ionic dissociation, the present intramolecular exciplex systems cannot dissociate. Instead, some of them show the solvent-induced electronic structural change, and they show a quite large red shift of exciplex fluorescence in the strongly polar solvents, in which the fluorescence of the intermolecular exciplex cannot be observed because of the ionic dissociation. Thus, restricting the geometrical structure of the exciplex system by connecting two moieties with the methylene chain, we have found some new phenomena which cannot be observed in the case of the strongly polar intermolecular exciplexes. Furthermore, the present results indicate clearly that the plane parallel sandwich structure is not necessary for the fluorescent exciplex in polar solvents.

For the more detailed elucidations of the behaviors of these intramolecular exciplexes, measurements of fluorescence quantum yields, rise and decay times, and $S_n \leftarrow S_1$ spectra are necessary. We have made such studies and the results will be reported in a separate paper.

References

1) See for example, (a) N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra," Marcel-Dekker Inc., New York, N. Y. (1970); (b) M. Ottolenghi, *Acc. Chem. Res.*, **6**, 153 (1973).

2) N. Mataga and Y. Murata, *J. Am. Chem. Soc.*, **91**, 3144 (1969); T. Kobayashi, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **44**, 2603 (1971); Y. Torihashi, Y. Furutani, K. Yagii, N. Mataga, and A. Sawaoka, *ibid.*, **44**, 2985 (1971).

3) K. Egawa, N. Nakashima, N. Mataga, and C. Yamanaka, *Chem. Phys. Lett.*, **8**, 108 (1971); *Bull. Chem. Soc. Jpn.*, **44**, 3287 (1971).

4) R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970); H. Masuhara and N. Mataga, *ibid.*, **6**, 608 (1970); H. Masuhara and N. Mataga, *Z. Phys. Chem. N. F.*, **80**, 113 (1972); H. Masuhara, N. Tsujino, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 1088 (1973); N. Tsujino, H. Masuhara, and N. Mataga, *Chem. Phys. Lett.*, **21**, 301 (1973); H. Masuhara and N. Mataga, *ibid.*, **22**, 305 (1973).

5) H. Masuhara, M. Shimada, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **43**, 3316 (1970); H. Masuhara, M. Simada, N. Tsujino, and N. Mataga, *ibid.*, **44**, 3310 (1971); M. Shimada, H. Masuhara, and N. Mataga, *Chem. Phys. Lett.*, **15**, 364 (1972); M. Shimada, H. Masuhara, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 1903 (1973).

6) H. Masuhara, N. Tsujino, and N. Mataga, *Chem. Phys. Lett.*, **12**, 481 (1972); N. Tsujino, H. Masuhara, and N. Mataga, *ibid.*, **15**, 357 (1972).

7) N. Mataga, T. Okada, and N. Yamamoto, *Bull. Chem. Soc. Jpn.*, **39**, 2562 (1966); *Chem. Phys. Lett.*, **1**, 119 (1967).

8) H. Knibbe, K. Röllig, F. P. Schäfer, and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967).

9) E. Lippert, *Z. Naturforsch.* **10a**, 541 (1955); N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **28**, 690 (1955).

10) E. A. Chandross and H. T. Thomas, *Chem. Phys., Lett.*, **9**, 397 (1971).

11) N. Mataga, Y. Torihashi, and K. Ezumi, *Theor. Chim. Acta (Berl)*, **2**, 158 (1964): N. Nakashima and N. Mataga, *Bull. Chem. Soc. Jpn.*, **46**, 3016 (1973).

12) Y. Taniguchi, Y. Nishina, and N. Mataga, *Bull. Chem. Soc. Jpn.*, **45**, 764 (1972): Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

13) F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **72**, 1155 (1968).

14) F. Schneider and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, **74**, 624 (1970); H. Beens and A. Weller, *Chem. Phys. Lett.*, **3**, 666 (1969).

15) N. Nakashima, M. Murakawa, and N. Mataga, *Bull. Chem. Soc. Jpn.*, to be published. Picosencond Flash Spectroscopy of Solvent-Induced Intramolecular Electron Transfer in the Excited 9,9′-Bianthryl.

16) T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata, and S. Misumi, *Chem. Phys. Lett.*, **14**, 563 (1972).

17) H. Beens, Thesis, Free University of Amsterdam, Amsterdam, 1970.

18) S. Yomosa, *J. Phys. Soc. Jpn.*, **35**, 1738 (1973).

19) R. Ide, M. Tsutsui, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, to be published. Synthesis of Intramolecular Exciplexes Containing Condensed Aromatic Hydrocarbon and *N,N*-Dimethylaniline Moieties.

20) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. III, Interscience, New York (1955).

21) T. Okada, T. Fujita, and N. Mataga, *Z. Phys. Chem. N. F.*, to be published. Intramolecular Charge Transfer Interactions and Dynamic Behaviors of Excited *p*-(9′-Anthryl)-*N,N*-dimethylaniline.