

CHARGE AND ENERGY TRANSFER PROCESSES IN EXCITED AMINOESTERS

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Summary

Fluorescence quenching and exciplex emission observed in *N,N*-dimethylaminoalkyl and *N*-methyl-*N*-phenylaminoalkyl esters of 1- and 2-naphthoic acids, 9-anthoic acid and 1-pyrenoic acid were analysed with respect to their kinetic and thermodynamic features.

Kinetic data showed that the rate constants follow Marcus theory for electron transfer, and repolarization energies λ of 0.56 eV (cyclohexane) and 1.20 eV (acetonitrile) were determined. Thermodynamic data confirmed the charge transfer nature of excited state interactions in these systems. The exciplexes observed have dipolar moments μ^2/ρ^3 of 1.3 - 1.7 eV and energies of 2.6 - 2.9 eV which are larger than those of the intermolecular analogue systems (μ^2/ρ^3 in the range 0.5 - 2 eV and energies in the range 2.4 - 2.6 eV), possibly as a result of an increase in the chromophore-chromophore distances in intramolecular exciplexes.

The occurrence of simultaneous energy transfer processes in aromatic aminoesters was also proved. The rate constants of competing processes are almost identical in the pyrenoate derivative ($k_{et} \approx k_{ct} \approx 1.6 \times 10^{10} \text{ s}^{-1}$) but are reversed in the naphthoate and 9-anthroate derivatives ($k_{ct} = 2.0 \times 10^{10} \text{ s}^{-1}$, $k_{et} = 7 \times 10^8 \text{ s}^{-1}$ and $k_{ct} = 8.2 \times 10^9 \text{ s}^{-1}$, $k_{et} = 2.1 \times 10^{10} \text{ s}^{-1}$ respectively). Both transfer processes can be rationalized in terms of an activated mechanism.

1. Introduction

The formation of excited state complexes where aromatic or aliphatic amines participate as electron donors is a well-known phenomenon, and there are several examples of bichromophoric systems of the type $\text{Ar}(\text{CH}_2)_n\text{Am}$ ($\text{Am} \equiv \text{amine}$) which exhibit exciplex emission [1]. We have reported [2] the occurrence of intramolecular charge transfer phenomena in the aromatic aminoesters shown in Fig. 1 where the ester moiety is the acceptor and the amine acts as the donor. In these compounds excitation of either the aro-

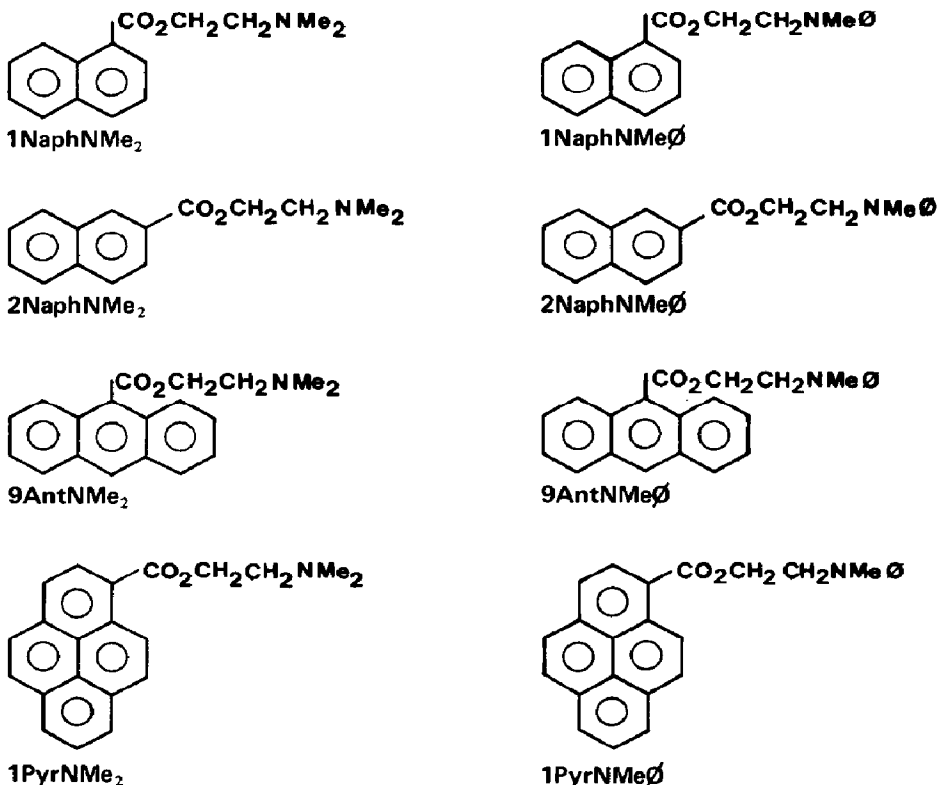


Fig. 1. Structures of aromatic aminoesters (Naph ≡ naphthalene; Me ≡ methyl; φ ≡ phenyl; Ant ≡ anthracene; Pyr ≡ pyrene).

matic amine or the ester leads to exciplex formation but energy transfer from the amine to the ester competes with charge transfer.

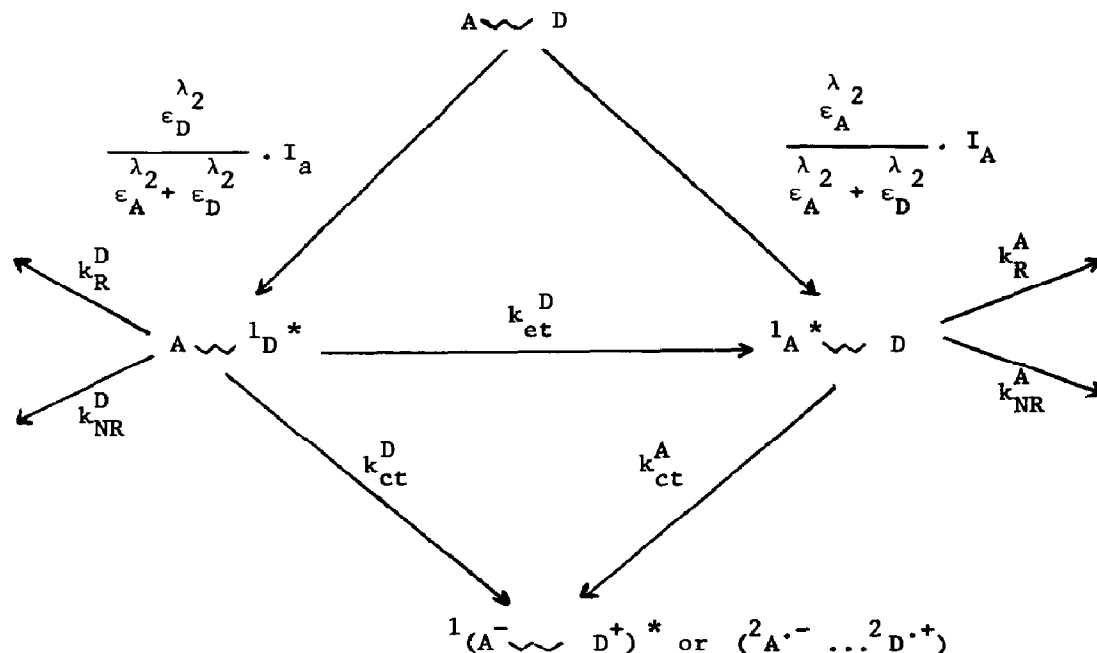
A time-resolved spectral study of the compound 2NaphNMeφ showed a significant static component in the fluorescence quenching as well as a slowly decaying component due to the diffusional approach of partners linked in the chain [3]. A separate analysis of the contribution of charge and energy transfer processes is given in this paper. A report of further studies on the mechanism of these intramolecular interactions supported by kinetic and thermodynamic evidence is therefore presented.

2. Results and discussion

2.1. Kinetics

The absorption spectra of all the aminoesters investigated show that they are additive with respect to chromophores and that excitation can be preferentially selected in either the acceptor (A) or the donor (D). The radiation of higher energy at wavelength λ_2 is absorbed by both chromophores, but at the longer wavelength λ_1 only $S_1(A)$ is excited. Therefore energy transfer from the excited amine to the ester ($E_{S_1(D)} > E_{S_1(A)}$), which competes with the charge transfer process, is observed.

Results obtained previously [2] have led us to propose the mechanism shown in the following scheme for the aminoester interaction:



$A \sim D$ refers to the intramolecular compound in the ground state, $A \sim D^*$ is the intramolecular compound in which the amine is excited, $A^* \sim D$ is the intramolecular system in which the ester is excited, ${}^1(A^- \sim D^+)^*$ is the exciplex, $({}^2A^{\cdot-} \dots {}^2D^{\cdot+})$ is the solvated ion pair, k_{et}^D is the rate constant for energy transfer from D^* to A, k_{et}^A is the rate constant for charge transfer from D^* , k_{ct}^D is the rate constant for charge transfer from D^* , k_{ct}^A is the rate constant for charge transfer from A^* , k_R^D , k_{NR}^D , k_R^A and k_{NR}^A are the radiative and non-radiative rate constants from D^* and A^* , and $\epsilon_{D(A)}^{\lambda_1(\lambda_2)}$ is the molar extinction coefficient of D (A) at wavelengths λ_1 (λ_2).

This mechanism enables the kinetics of the charge and energy transfer processes involved to be studied separately. Studies of the variation in the exciplex-to-monomer fluorescence intensity ratio with temperature [2] showed that the hypothesis of charge transfer reversibility ${}^1(A^- \sim D^+)^* \rightarrow {}^1A^* \sim D$ could be neglected.

2.2. Steady state kinetics of charge transfer

At the excitation wavelength λ_1 the following steady state kinetic equation (Stern-Volmer law applied to unimolecular quenching) can be used to study the quenching of the emission ϕ from the aromatic compound compared with the emission ϕ_0 from the parent methyl ester:

$$\left(\frac{\phi_0}{\phi}\right)_{\lambda_1}^A = \left(\frac{I_{f_0}}{I_f}\right)_{\lambda_1} \frac{\epsilon_A^{\lambda_1} [AD]}{\epsilon_A^{\lambda_1} [A]} = 1 + k_{ct}^A \tau_0^A \quad (1)$$

TABLE 1

Fluorescence quantum yield ratios $(\phi_0/\phi)_{\lambda_1}^A$, lifetimes τ_0^A and charge transfer rate constants k_{ct}^A

Aminoester	Values obtained in cyclohexane			Values obtained in acetonitrile		
	τ_0^A a ($\times 10^{-9}$ s $^{-1}$)	$(\phi_0/\phi)_{\lambda_1}^A$ b	k_{ct}^A ($\times 10^8$ s $^{-1}$)	τ_0^A a ($\times 10^{-9}$ s $^{-1}$)	$(\phi_0/\phi)_{\lambda_1}^A$ b	k_{ct}^A ($\times 10^8$ s $^{-1}$)
1NaphNMe ₂	0.6	5.6	57.5	1.8	7.7	37.2
1NaphNMe ϕ		12.5	144		16.7	87.0
2NaphNMe ₂	15.5	17.0	10.3	10.2	8.3	7.2
2NaphNMe ϕ		243.9	156.7		83.3	80.6
1PyrNMe ₂	15.0	5.3	2.8	11.0	5.0	3.6
1PyrNMe ϕ		128.2	84.8		263.2	238.3
9AntNMe ₂	13.1	6.1	3.9	8.0	8.9	9.9
9AntNMe ϕ		52.6	39.4		83.3	102.9

^aFrom ref. 4.

^bFrom ref. 2.

where I_f and I_{f_0} are the fluorescence intensities of the aromatic aminoester and the parent methyl ester respectively, $[AD]$ and $[A]$ are the concentrations, τ_0^A is the singlet lifetime of the parent compound and k_{ct}^A is the charge transfer rate constant for the excitation of the ester moiety. The values of k_{ct}^A , $(\phi_0/\phi)_{\lambda_1}$ and τ_0^A are given in Table 1.

The rate constants should obey the Marcus equation [5]

$$k_{ct}^A = k_0 \exp\left(-\frac{\Delta G_A^\ddagger}{k_B T}\right) \quad (2)$$

where k_0 is the pre-exponential factor and the energy of activation ΔG_A^\ddagger for exothermic transfers is related to the free energy ΔG_A^0 associated with the charge transfer process and the repolarization energy λ by the empirical equation

$$\Delta G^\ddagger = \left\{ \left(\frac{\Delta G^0}{2} \right)^2 + \left(\frac{\lambda}{4} \right)^2 \right\}^{1/2} + \frac{\Delta G^0}{2} \quad (3)$$

proposed by Rehm and Weller [6].

The free energies ΔG_e^0 and ΔG_p^0 of exciplex formation (cyclohexane) and ion pair formation (acetonitrile) respectively can be determined using the equations [7]

$$\Delta G_e^0 = E_{D|D^+} - E_{A^-|A} - h\nu_0^A + 0.36 \text{ eV} \quad (4)$$

$$\Delta G_p^0 = E_{D|D^+} - E_{A^-|A} - h\nu_0^A - 0.06 \text{ eV} \quad (5)$$

TABLE 2

Free-energy changes ΔG_e^0 and ΔG_p^0 of the exciplexes and the ion pairs respectively and the redox potentials $E_{D|D^+} - E_{A^-|A}$

<i>Aminoester</i>	$E_{D D^+} - E_{A^- A}$ ^a (eV)	ΔG_e^0 (eV)	ΔG_p^0 (eV)
1PyrNMe ₂	2.84	-0.02	-0.44
1PyrNMe ϕ	2.21	-0.65	-1.07
9AntNMe ₂	2.83	+0.05	-0.37
9AntNMe ϕ	2.20	-0.58	-1.00
1NaphNMe ₂	3.17	-0.32	-0.74
1NaphNMe ϕ	2.54	-0.95	-1.37
2NaphNMe ₂	3.21	-0.14	-0.56
2NaphNMe ϕ	2.58	-0.77	-1.19

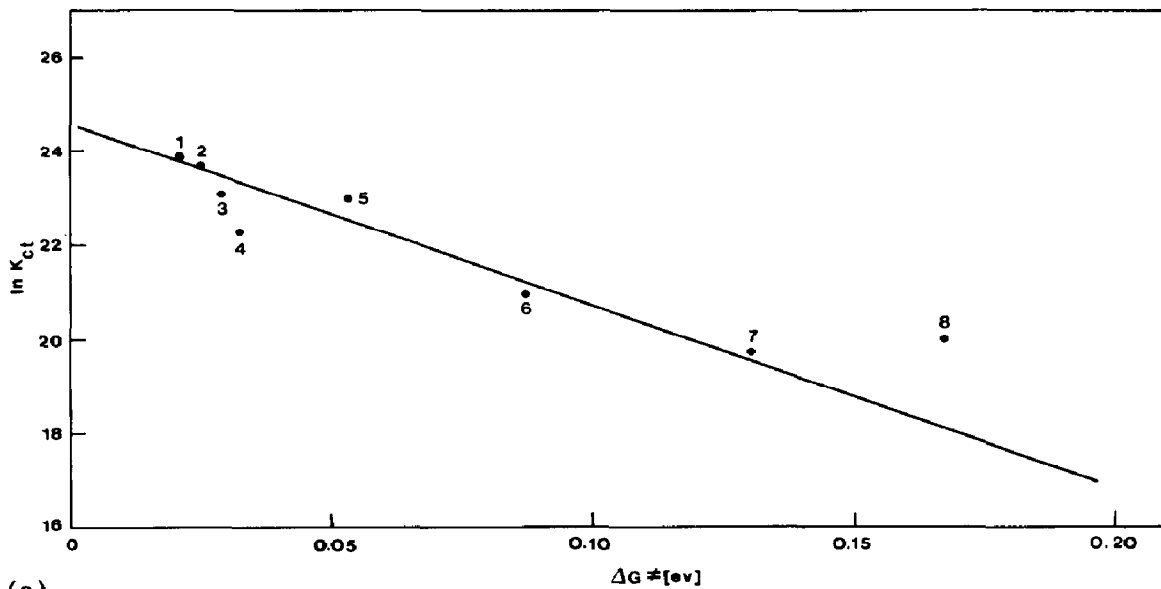
^a $E_{D|D^+}$ is calculated from $E_{D|D^+} = I_D - 6.3$ eV [7, 8] and $E_{A^-|A}$ is taken from ref. 9.

and are shown in Table 2 together with values of the redox potentials $E_{D|D^+} - E_{A^-|A}$.

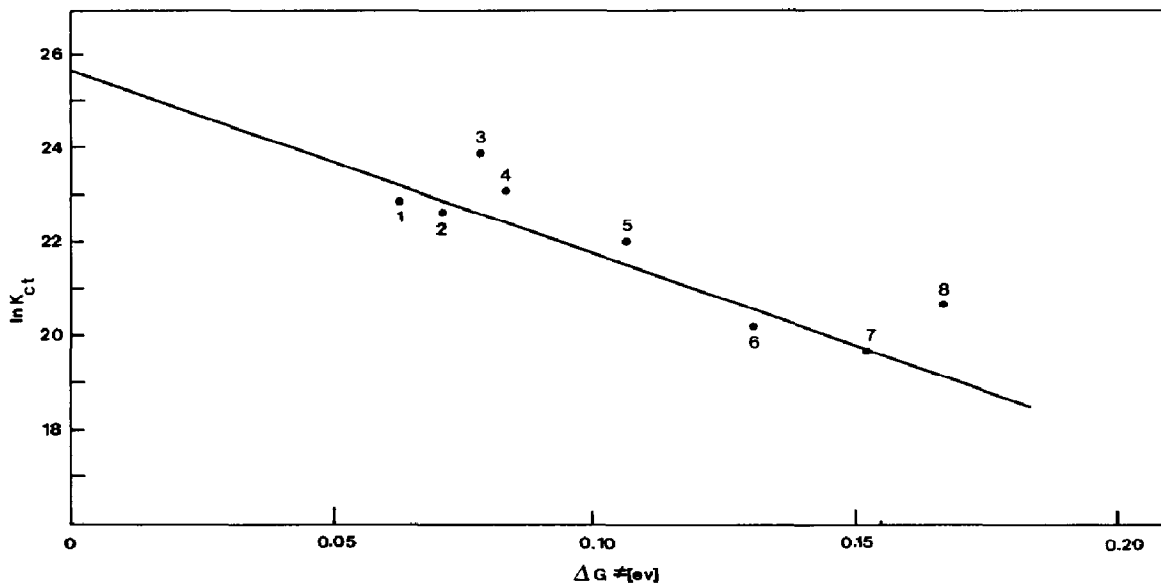
The plots presented in Fig. 2 were determined by fitting eqn. (3) to the slope $1/k_B T$ expected from eqn. (2). The experimental data follow the predicted linear relation reasonably well, except for the systems containing the anthroate chromophore, possibly because of the large structural changes which accompany the excitation process [7, 10].

The values of the repolarization energies $\lambda = 0.56$ eV (cyclohexane) and $\lambda = 1.20$ eV (acetonitrile) are in good agreement with those obtained in the corresponding intermolecular systems (0.64 eV and 1.08 eV respectively [7]). No values have been reported in the literature for non-polar media, but those reported in studies of charge transfer in polar solvents [6, 11 - 13] are lower than those obtained in this study. However, the published values are averaged over several systems and therefore do not distinguish between aliphatic and aromatic amine derivatives, which are expected to have rather different repolarization energies [12, 14]. The pre-exponential factors obtained are $k_0 = 4.0 \times 10^{10} \text{ s}^{-1}$ (cyclohexane) and $k_0 = 1.5 \times 10^{11} \text{ s}^{-1}$ (acetonitrile). These values are an order of magnitude smaller than the corresponding values obtained with the equivalent intermolecular systems [7] and may reflect a distance dependence which has not been considered in this study as well as a different electronic matrix element.

Indeed, this kinetic model is oversimplified since the total population of conformers is described in terms of only one conformer and consequently ignores the conformational aspects relevant to the mechanism.



(a)



(b)

Fig. 2. Dependence of $\ln k_{ct}$ on ΔG^\ddagger in (a) cyclohexane and (b) acetonitrile: point 1, 1NaphNMe ϕ ; point 2, 2NaphNMe ϕ ; point 3, 1PyrNMe ϕ ; point 4, 9AntNMe ϕ ; point 5, 1NaphNMe $_2$; point 6, 2NaphNMe $_2$; point 7, 1PyrNMe $_2$; point 8, 9AntNMe $_2$.

2.3. Steady state kinetics of energy transfer

It can easily be demonstrated from the mechanism proposed in Section 2.1 that the application of steady state kinetics to the excitation of both A and D at λ_2 leads to the equation

TABLE 3

Energy transfer efficiencies γ_{et} , charge transfer rate constant k_{ct}^D , energy transfer rate constants k_{ct}^A , spectral overlap integral J' and critical Förster radius R_0

Aminoester	γ_{et}	k_{ct}^D ($\times 10^9$ s $^{-1}$)	k_{ct}^A ($\times 10^9$ s $^{-1}$)	J' ($\times 10^{-4}$ cm)	R_0 (Å)
2NaphNMe ϕ	0.03	20.3	0.7	2.203	10.6
1PyrNMe ϕ	0.51	16	17.1	1.317	24.8 ^a
9AntNMe ϕ	0.71	8.2	21.1	1.759	19.8

^aFrom ref. 17.

$$\left(\frac{\phi_0}{\phi}\right)_{\lambda_2}^A = \left(\frac{I_{f_0}}{I_f}\right)_{\lambda_2} \frac{\epsilon_A^{\lambda_2}[AD] + \epsilon_D^{\lambda_2}[AD]\gamma_{et}}{\epsilon_A^{\lambda_2}[A]} = 1 + k_{ct}^A \tau_0^A \quad (6)$$

where γ_{et} is the energy transfer efficiency defined by

$$\gamma_{et} = \frac{k_{ct}^D}{k_{et}^D + k_{ct}^D + 1/\tau_0} \quad (7)$$

Combination of eqns. (6) and (1) leads to the equation

$$\frac{(I_{f_0}/I_f)_{\lambda_1}}{(I_{f_0}/I_f)_{\lambda_2}} - 1 = \frac{\epsilon_D^{\lambda_2}}{\epsilon_A^{\lambda_2}} \gamma_{et} \quad (8)$$

which enables an experimental determination of γ_{et} to be made.

The rate constant k_{ct}^D for charge transfer from D^* can be calculated from k_{ct}^A if the amount of energy $h\nu_D$ corresponding to the excitation involved is taken into account in the estimation of ΔG_D^{\ddagger} (eqn. (3)). Therefore, since the pre-exponential factor remains constant, the following equation is obtained by using Marcus's formalism [5]:

$$k_{ct}^D = k_{ct}^A \exp\left\{-\left(\frac{\Delta G_D^{\ddagger} - \Delta G_A^{\ddagger}}{k_B T}\right)\right\} \quad (9)$$

The efficiencies γ_{et} and the rate constants k_{ct}^D and k_{ct}^A are presented in Table 3 together with the parameters J' and R_0 obtained from the exchange (Dexter) [15] and dipolar (Förster) [16] mechanisms respectively.

On account of the low absorptivities observed, a trivial radiative process [18, 19] is not important in these systems. However, if either exchange or dipolar mechanisms are operative, the rate constants are proportional to the overlap integral J' or the critical Förster radius R_0 ; the chromophore distances are the same in all systems. The magnitudes and the trends in the variation in these parameters differ from those predicted for k_{ct}^D . Values of 9.8 Å, 10.6 Å and 13.8 Å were obtained for chromophore distances in 2NaphNMe ϕ , 9AntNMe ϕ and 1PyrNMe ϕ respectively using Förster theory. These values are inconsistent and are much larger than expected even for the maximum chain length.

TABLE 4

Free energies ΔE and activation energies ΔE^\ddagger for the energy transfer step

	$-\Delta E$ (eV)	ΔE^\ddagger (eV)
2NaphNMe ϕ	0.19	0.074
1PyrNMe ϕ	0.67	0.028
9AntNMe ϕ	0.65	0.029

A new formalism, which has strong analogies with that used for electron transfer processes, has recently been introduced to evaluate energy transfer rate constants [20]. However, the variation in the free energy associated with the energy transfer process is the difference between the spectroscopic energies E_{0-0} of the electronic excited states of the donor and acceptor ($\Delta E^0 = h\nu_D - h\nu_A$). These energies, together with the activation energies calculated using $\lambda = 0.56$ eV, are presented in Table 4.

Values of k_{et}^D calculated using

$$k_{et}^D = k_0 \exp\left(-\frac{\Delta E^\ddagger}{k_B T}\right) \quad (10)$$

agree very well with the experimental values presented in Table 3. Consequently, an activation mechanism may be applicable in these systems.

Energy transfer studies in intramolecular systems are difficult because of the molecular restrictions such as distances and orientation. Therefore the Förster mechanism cannot be excluded here because the dipolar orientation is not known and a random value has been used. Furthermore, the study presented here is not exhaustive but has only attempted to verify the main pathway for energy transfer.

2.4. Thermodynamics of charge transfer

The charge transfer nature of emissive states can be demonstrated by comparing the observed exciplex energies with those calculated using the equation [21]

$$E(\text{CT}) = E_{D|D^+}(\text{DMF}) - E_{A^-|A}(\text{DMF}) - \Delta\Delta G_S + C(D^+, A^-) - \Delta C(D^+, A^-) + \Delta G_E^{\text{sol}}(S) - E_R \quad (11)$$

where $E_{D|D^+}(\text{DMF})$ and $E_{A^-|A}(\text{DMF})$ are the redox potentials in dimethylformamide, $C(D^+, A^-)$ is the coulombic interaction term and E_R is the repulsion energy. The other terms are corrective terms required to account for solvent effects and they were calculated using $C(D^+, A^-) = -3.3$ eV [22] and $E_R = 0.20$ eV [23] obtained from intermolecular systems and $R_{D^+} = 3.1$ Å and $R_{A^-} = 3.9$ Å [7]. Substitution of these values leads to

TABLE 5

Experimental and calculated exciplex emission energies $E(\text{CT})_{\text{exp}}$ and $E(\text{CT})_{\text{calc}}$

System	$E(\text{CT})_{\text{exp}}$ (eV)	$E(\text{CT})_{\text{calc}}$ (eV)
<i>Intermolecular</i>		
1Pyr- ϕNMe_2	2.43	2.19
9Ant- ϕNMe_2	2.21	2.18
1Naph- ϕNMe_2	2.29	2.52
2Naph- ϕNMe_2	2.53	2.56
Ant- ϕNMe_2	2.60	2.66
<i>Intramolecular</i>		
1PyrNMe ϕ	2.62	2.14 (2.54)
9AntNMe ϕ	2.70	2.13 (2.53)
1NaphNMe ϕ	2.79	2.47 (2.87)
2NaphNMe ϕ	2.90	2.51 (2.91)

$$E(\text{CT}) = E_{\text{D}|\text{D}^+} - E_{\text{A}^-|\text{A}} - 0.07 \text{ eV} \quad (12)$$

The experimental and calculated exciplex emission energies for intramolecular and intermolecular systems are presented in Table 5. Examination of this table shows that the orders of magnitude and the trends in the variation in experimental exciplex emission energies observed are correctly predicted, thus confirming the charge transfer nature of the emissive state.

However, whereas the experimental energies found for the intermolecular systems are in good agreement with the calculated values, they are 0.45 eV larger for the intramolecular systems investigated here. Therefore assumptions made for the intermolecular systems may not be valid for the intramolecular systems.

The restrictions imposed on the exciplex relaxation by the chain are due to the larger equilibrium distance between A^- and D^+ compared with that in intermolecular exciplexes. Consequently both the coulombic interaction energy $C(\text{A}^-, \text{D}^+)$ and the repulsion energy E_{R} should decrease and a blue shift should be observed (Fig. 3). Indeed, an increase of 0.5 - 1 Å in the distance between two chromophores in the intramolecular exciplex reduces the coulombic term by 0.3 eV [22]. The $E(\text{CT})$ values calculated when E_{R} is reduced by 0.1 eV are given in parentheses in Table 5. Changes in the exciplex geometry may also be responsible for a significant alteration in its emission energy [24].

The dipolar moments of the intramolecular exciplexes are also larger than those of the equivalent intermolecular exciplexes (Table 6). This result, which was also obtained by Meeus *et al.* [25] for naphthalene-piperidine systems, appears to be consistent with the hypothesis of an increase in the chromophore-chromophore distance proposed above.

It was not possible to detect the radicals (or ion pairs) in the polar medium (acetonitrile) within the time resolution used because of their rapid

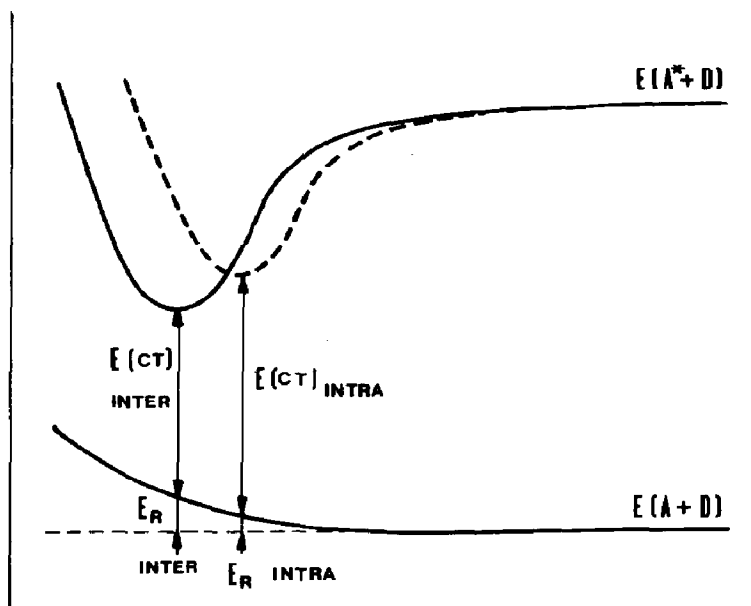


Fig. 3. Potential energy diagram of intermolecular and intramolecular exciplexes.

TABLE 6

μ^2/ρ^3 values for intramolecular and intermolecular systems

Ester	μ^2/ρ^3 (eV) for the following systems	
	Intramolecular system (ester-NMe ϕ)	Intermolecular system (ester-Et $_3$ N)
2Naph	1.76	2.05
1Naph	1.41	0.80
1Pyr	1.31	0.49

TABLE 7

Ratio ϕ_p/ϕ_f of phosphorescence to fluorescence quantum yields and phosphorescence lifetimes τ_p at 77 K

Parameter	Solvent	2Naph	2NaphNMe $_2$	2NaphNMe ϕ
ϕ_p/ϕ_f	Methylcyclohexane	0.004	—	1.4
τ_p (s)	Methylcyclohexane	2.65	2.40	2.25
ϕ_p/ϕ_f	Ethanol	0.087	0.13	91

recombination. However, these systems provide direct spectroscopic evidence for a charge transfer interaction. An exciplex emission is observed in ethanol at 77 K [2] and the ratio of phosphorescence to fluorescence quantum yields is intensified (Table 7).

The spin-orbit coupling induced by exciplex formation [26] or radical recombination [27 - 29] is well established. The latter is illustrated here by the difference between the results obtained in the non-polar solvent (methylcyclohexane) and in the polar solvent (ethanol). The quasi-invariability of τ_p also shows that the triplet state is not involved in the interaction with the amine.

3. Conclusion

The work presented here demonstrates the simultaneous occurrence of charge and energy transfer processes following the population of an excited state, as has been observed in other systems [30]. An activated mechanism involving the same formal dependence of activation energies may rationalize the competition of transfer processes. Simple kinetic and thermodynamic data reflect the importance of restrictions imposed by the linking chain in intramolecular systems which leads to larger approach distances than are obtained in intermolecular systems. A detailed study of the mechanism of these interactions using both steady state and transient kinetics is in progress and will be presented in a forthcoming publication.

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