INTRAMOLECULAR EXCITED STATE INTERACTIONS IN AMINO-ESTERS

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Summary

N,N-Dimethylaminoalkyl and N-methyl-N-phenylaminoalkyl esters of 1- and 2-naphthoic acid, 9-anthroic acid and 3-pyrenoic acid exhibit excited intramolecular charge transfer interactions which lead to quenching of the fluorescence of the ester. In these bichromophoric systems excitation of either the aromatic amine or the hydrocarbon group leads to fluorescent exciplex formation, the ratio of exciplex-to-monomer intensities being greater when the amine is excited.

The exciplex emission was also detected at 77 K, both in polar and non-polar solvents, suggesting that the interaction in these systems is of a dynamic type but also has a static contribution.

In these systems transfer of amine excitation to the ester competes with direct exciplex formation from the aromatic amine.

1. Introduction

Since Chandross and Thomas [1] and Brimage and Davidson [2] reported the formation of intramolecular amine hydrocarbon exciplexes, this topic has received much attention and has recently been reviewed [3].

The geometrical requirements for exciplex formation do not seem to be as stringent as those in excimers [4], and it is generally observed that in bichromophoric systems of the type $Ar(CH_2)_n Am$ the exciplex is formed when $n = 2$ or 3 [5]. The extension of the linking chain with the introduction of a carboxyl group did not prevent exciplex formation or significantly alter the properties of the exciplex [6].

Continuing our programme of studies on the interaction between aromatic esters and amines in the excited state [7, 8] we have investigated the compounds I, II, III and IV (Fig. 1) in order to compare them with

$X = CO_2(CH_2)_2 \; N \overset{R_1}{\underset{R_2}{\diagdown}}$

a) R_1, R_2 = Me
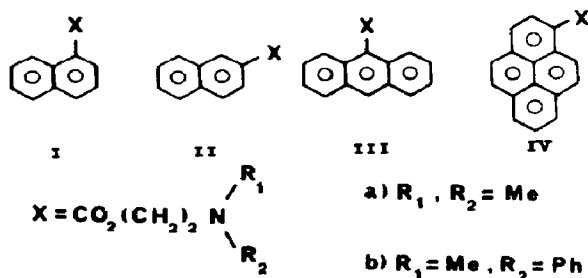
b) R_1 = Me, R_2 = Ph

Fig. 1. Structure of compounds I - IV.

intermolecular systems, thus using exciplex formation as a probe for studies related to electron transfer in this type of compounds.

2. Experimental

The aminoesters I(a) and I(b) - IV(a) and IV(b), where (a) refers to the N,N-dimethylamino esters and (b) refers to the N-methyl-N-phenylamino esters, were synthesized by direct reaction of the corresponding amino-alcohols with the acyl chlorides. The purity of the compounds was checked using infrared spectroscopy and nuclear magnetic resonance spectroscopy.

The absorption spectra were recorded in a Hitachi 124 Perkin−Elmer spectrophotometer in 1 cm quartz cells. The corrected emission spectra of degassed solutions were recorded in an MPF-3 Perkin−Elmer spectrofluorimeter. The spectra at 77 K were obtained using the phosphorescence accessory without the chopper.

3. Results and discussion

Because the intensity of monomer fluorescence increases linearly in the concentration range 2×10^{-5} - 4.5×10^{-4} M, no intermolecular interaction occurs at the aminoester concentration of 10^{-4} M which was used throughout this work. In all these systems the absorption spectrum is additive for each chromophore and indicates no interaction in the ground state.

Excitation of compounds I(a) - IV(a) leads in all cases to fluorescence which is caused entirely by the aryl ester. For all the compounds studied the quantum yield of the emission is less than that for the parent methyl esters. Moreover, in non-polar solvents the monomer emission of compounds I(b), II(b) and IV(b) is accompanied by a structureless emission which is attributed to an exciplex and no emission from the aromatic amine chromophore is apparent. In contrast with the intermolecular interaction of 9-anthroate ester with dimethylaniline [9] there is no clear evidence for an intramolecular exciplex in compound III(b), since the very weak tail which is observed

underneath the monomer emission does not shift when the polarity of the solvent is very slightly increased.

The lack of exciplex emission in compounds I(a) - IV(a) may be related to conformational factors. Indeed, in these compounds the interaction of the nitrogen lone pair has a directional character and its overlap with the aromatic π system may be subject to some geometrical restrictions, introduced by the σ bond framework of the methylene chain, which are not favourable to the formation of an emissive exciplex. In the series of compounds I(b), II(b) and IV(b) these geometrical restrictions become less important. The aromatic amine has a lower ionization potential, and a larger spatial interaction results from the overlap of the aromatic π systems of the donor and the acceptor.

The dipole moments of the exciplexes were determined using the system anthracene–diethylaniline ($\mu_R = 10$ debye and $a_R = 5$ Å) [10] as a reference in order to correct for the specific exciplex–solvent interactions. The results are shown in Fig. 2 and from the linear correlations obtained it is possible to estimate μ_E using

$$\tilde{\nu}_E = \frac{\mu_E^2 a_R^3}{\mu_R^2 a_E^3} \tilde{\nu}_R - \left\{ \frac{\mu_E^2 a_R^3}{\mu_R^2 a_E^3} \tilde{\nu}_R(0) - \tilde{\nu}_E(0) \right\} \tag{1}$$

where the indexes E and R refer to the unknown exciplex and the reference system respectively and $\tilde{\nu}$, μ and a have their usual meanings.
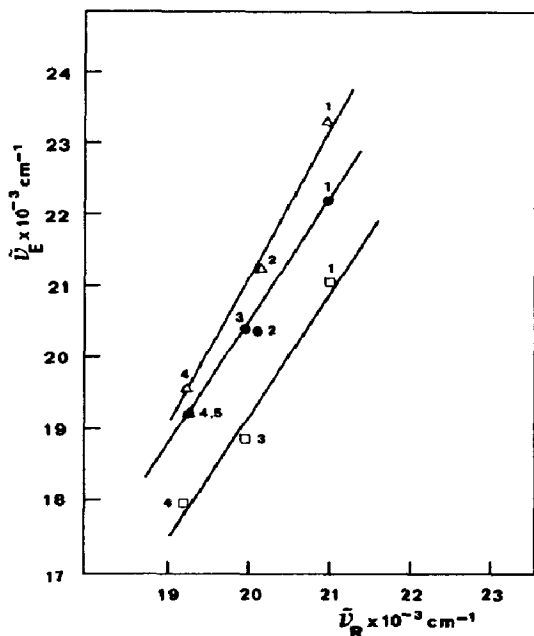

Fig. 2. The variation of the maximum wavenumber of the exciplexes I(b), ●; II(b), △; IV(b), □ with the maximum wavenumber of the reference exciplex. The solvents used were: 1, hexane; 2, diethyl ether; 3, benzene; 4, chloroform; 5, ethyl acetate.

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Dipole moments of exciplexes in compounds I(b), II(b) and IV(b)

Compound	a (Å)	μ_E (debye)	a (Å)	μ_E (debye)	a (Å)	μ_E (debye)
I(b)	4.5	13.3	5.0	15.6	5.5	17.9
II(b)	4.5	17.0	5.0	19.9	5.5	22.9
IV(b)	5.0	13.4	5.5	15.4	6.0	17.6

The values obtained are listed in Table 1 for several Onsager radii (because of the uncertainty of this parameter), and they show a substantial charge separation in the exciplex. The calculated value for a full electron transfer in the naphthalene triethylamine exciplex is 16.8 debye [11], indicating the very strong charge transfer nature of the donor–acceptor interactions in these and similar systems [8].

In these systems, although it is impossible to excite each chromophore selectively when the amine moiety is aromatic, it is possible to excite one of them "preferentially". Of all the compounds studied in this work, II(b) has the best separation of the absorptions due to each chromophore and allows a selective excitation of the naphthoate group at a wavelength λ of 280 nm and a preferential excitation of the amine chromophore at λ = 255 nm (Fig. 3).

Similar to intermolecular systems [12], the selective excitation of each chromophore leads to exciplex formation. Figure 4 shows the exciplex emissions obtained for different excitation wavelengths and with the monomer emission normalized. It can be seen that when the excitation is essentially
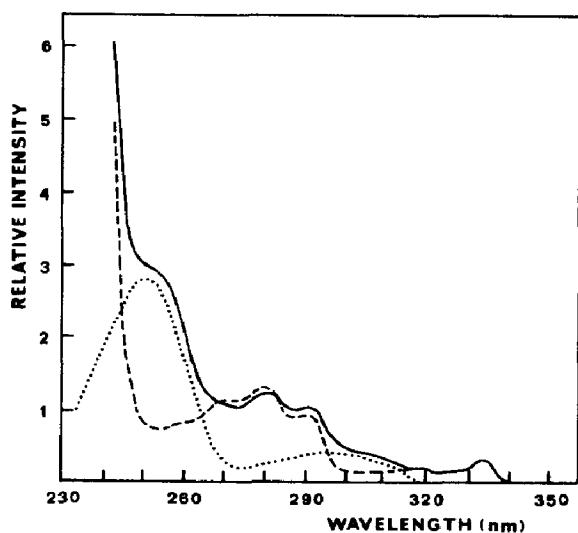

Fig. 3. Absorption spectra in ethanol: ———, compound II(b); — — —, methyl 2-naph-thoate; · · ·, dimethylaniline.
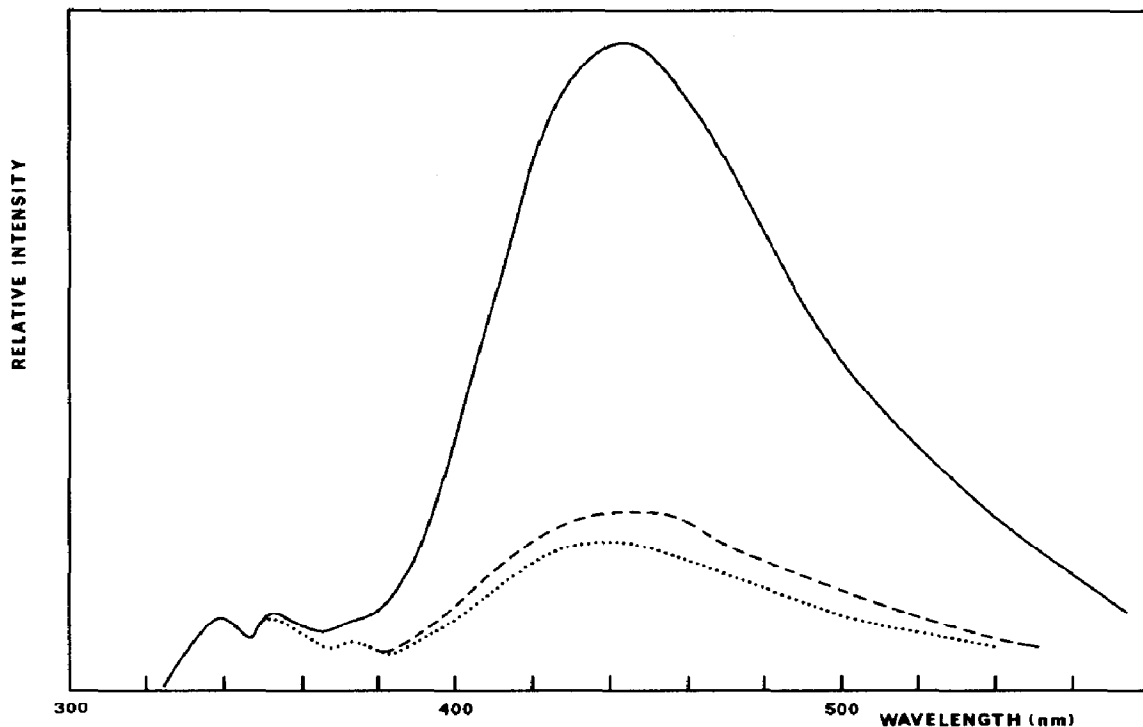
Fig. 4. Emission spectra of compound II(b) in cyclohexane at different exciation wavelengths: ———, λ_{ex} = 255 nm; — — —, λ_{ex} = 240 nm; · · ·, λ_{ex} = 280 nm.

associated with the amine, the ratio I_E/I_M of the exciplex emission to the monomer emission is dramatically increased, suggesting a strong contribution of the amine to the formation of the exciplex. The same conclusion can be drawn from Fig. 5 since the excitation spectrum of the monomer does not coincide with the excitation spectrum of the exciplex, the differences lying in the region of the amine absorption.

In Table 2 the absolute quantum yields of monomer emission are compared with those of the parent compounds. The values indicate that the parent ester emission is strongly quenched by both amines but that this effect is more pronounced for the aromatic amine, in agreement with its lower ionization potential. They also show that the ratio of the quantum yields of the parent methyl esters to those for the monomer emission of the aminoesters is higher in compound II(a) for the N,N-dimethylamino esters and in compounds II(b) and IV(b) for the N-methyl-N-phenylamino esters. These differences can be fully explained only by taking into account the lifetimes of the different esters involved and the kinetics of this interaction, which we will discuss in a separate publication.

The quenching of the monomer emission in ethanol in compounds I(b) and II(b) is similar to that observed in acetonitrile, whereas in compounds I(a) and II(a) the quenching in ethanol is much less effective. This inefficiency in quenching may be attributed to the involvement of the nitrogen atom in
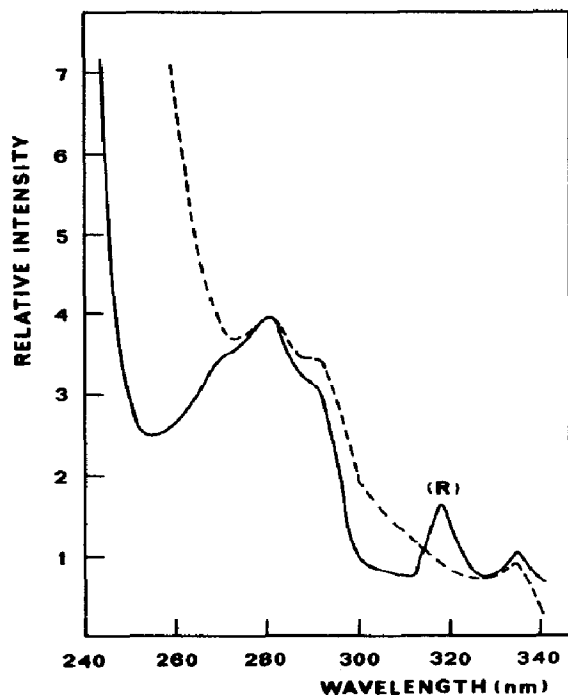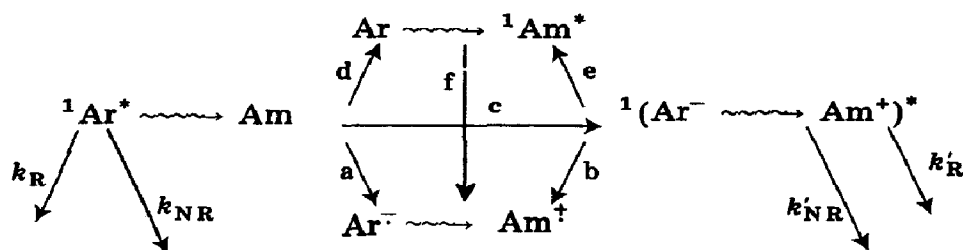
Fig.5. Excitation spectra of compound II(b) in cyclohexane at different emission wavelengths: ———, λ_{em} = 350 nm; — — —, λ_{em} = 440 nm. (R) is a Raman peak.

the formation of hydrogen bonds in protic solvents rather than to the long dielectric relaxation time of alcohols [14], since this effect is not observed when the amine is aromatic.

The results obtained can be explained using Scheme 1.

Scheme 1.

In polar solvents the exciplex emission is not generally detected at room temperature since the free energy of the radical ion pair will be lower than the free energy of the exciplex [15] (steps a and f in Scheme 1). Also the exciplex dissociates rapidly into radical ions because of the stabilization induced by the solvent (step b in Scheme 1).

In contrast, in ethanol at 77 K an exciplex emission was detected and is shown in Fig. 6. This behaviour can be explained on thermodynamic

TABLE 2

Fluorescence quantum yields of compounds I(a) and I(b) - IV(a) and IV(b) ϕ_f and of the corresponding methyl esters ϕ_f^o

Solvent[a]	$\phi_f^{o\,b}$	Parent compound	Compound	ϕ_f^{b}	
				(a)	(b)
Cyclohexane	0.04	Methyl 1-naphthoate	I	0.0072	0.0032
Ethanol	0.28			0.056	0.0084
Acetonitrile	0.20			0.026	0.012
Cyclohexane	0.32	Methyl 2-naphthoate	II	0.019	0.0013
Ethanol	0.36			0.202	0.0016
Acetonitrile	0.34			0.041	0.0041
Cyclohexane	0.85[c]	Methyl 9-anthroate	III	0.14	0.016
Acetonitrile	0.41[c]			0.046	0.0048
Cyclohexane	0.91	Methyl 3-pyrenoate	IV	0.173	0.0071
Acetonitrile	0.46			0.092	0.0017

[a]Degassed solutions.　[b]λ_{exc} = 280 nm.　[c]Data taken from ref. 13.

grounds. In photoassociation processes the entropy variation is significantly more negative for exciplex formation than for the formation of radical ion pairs, since the conformational requirements for exciplex formation are more stringent than those for radical ion pair formation where the interactions are purely electrostatic. However, at low temperatures the stabilization enthalpy of the radical ion pair by the solvent will be reduced because of the long dielectric relaxation time of ethanol. Therefore under these conditions, step c or step e will be more favoured than steps a and f in Scheme 1.
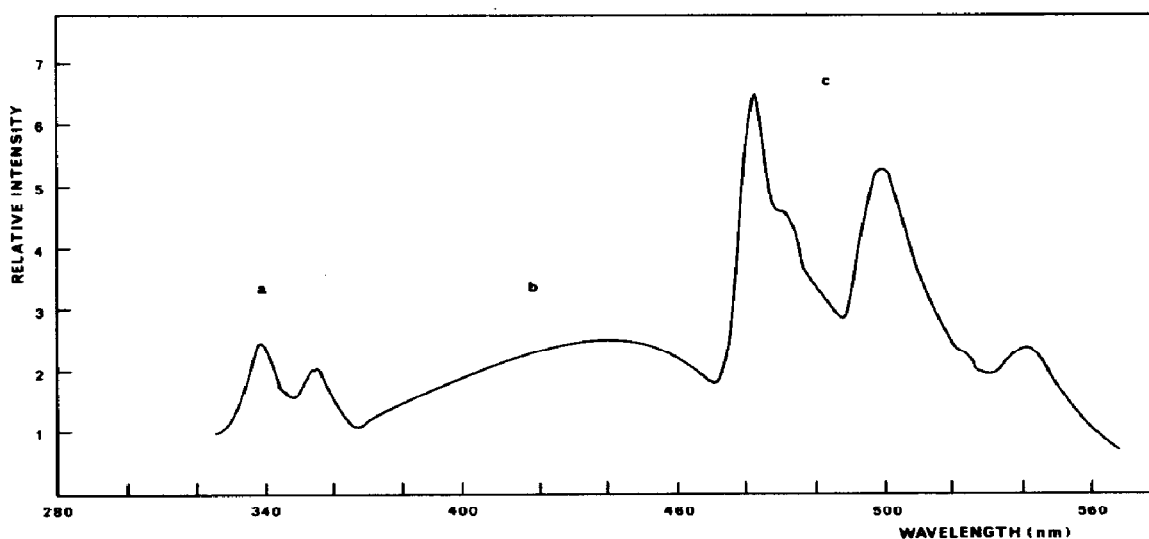

Fig. 6. Emission spectrum of compound II(b) in ethanol at 77 K and λ_{ex} = 280 nm: a, monomer fluorescence; b, exciplex emission; c, phosphorescence.

The quantum yield of exciplex formation increases at low temperatures because of the decrease in the rate constant of process b in Scheme 1, and thus the radiative process becomes more competitive. The fact that the exciplex emission in ethanol at 77 K is observed at the same energy as the emission in cyclohexane confirms that there is no stabilization induced by the solvent.

This emission is also observed in non-polar solvents at 77 K (Fig. 7), and suggests the occurrence of static quenching which implies that some molecules have the geometrical requirements for exciplex formation without diffusion.

Whilst there is no evidence from the absorption spectra of any inter-action in the ground state, the shift of 2 nm observed with respect to the parent methyl ester is probably associated with a polar environment which is created when the amino group is positioned over carbon 2 of the naph-thalene nucleus in a frozen conformation.

A comparison of the quenching efficiencies of the monomer emission measured at 77 K and at room temperature (Fig. 8) shows that the interaction of the two chromophores is not purely dynamic [16] (folding of the molecular chain allowing contact between the chromophores), but also has some static contribution which is likely to occur through space rather
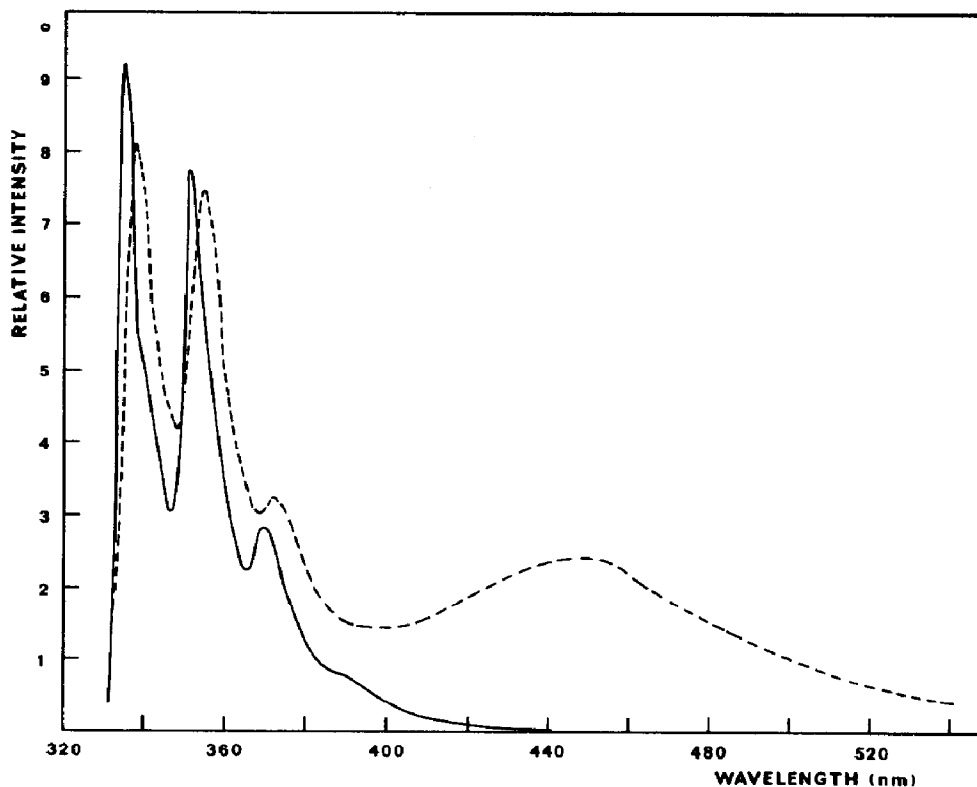

Fig. 7. Emission spectra in methylcyclohexane at 77 K and λ_{ex} = 280 nm: ————, methyl 2-naphthoate; — — —, compound II(b).
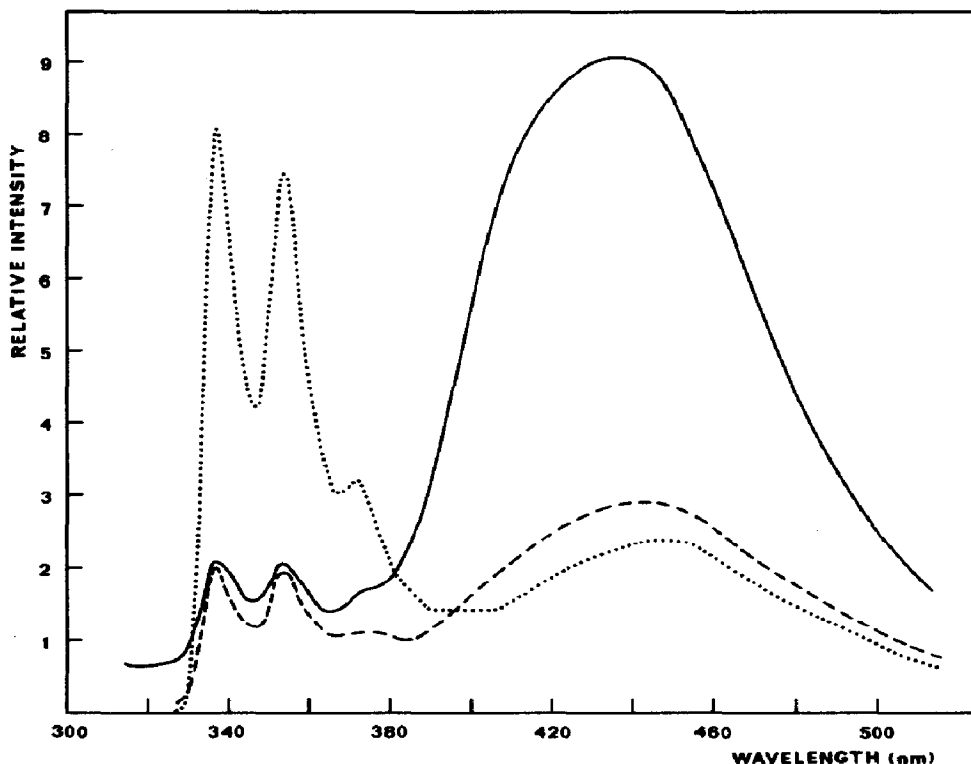
Fig. 8. Emission spectra of compound II(b) in methylcyclohexane: · · ·, λ_{ex} = 280 nm, 77 K; ———, λ_{ex} = 280 nm, 298 K; — — —, λ_{ex} = 255 nm, 77 K.

than through bonds [17]. However, the higher quantum yields observed for the exciplex emission at room temperature suggest that there are some conformational restrictions for its formation.

The spectral evidence obtained for compounds II(b) and III(b) from the excitation spectra of the monomer indicates some contribution of the aromatic amine; this is consistent with an energy transfer mechanism from the excited amine to the ester since no such contribution is detected in the excitation spectra of the parent compound. However, since the excitation spectra from the exciplex in all these systems show a large amine contribution we conclude that both phenomena, electron transfer and energy transfer, can compete (steps d and e in Scheme 1).

The variation of the exciplex-to-monomer intensity ratio with temperature (low and high) [18] shows a linear correlation without any inflection, indicating that reversibility of the exciplex cannot account for the excited monomer [12].

It may also be considered that because the excited amine has a very low ionization potential it can eject an electron, thereby decreasing the energy barrier for electron transfer to the acceptor and possibly increasing the rate of exciplex formation. Whilst the effect observed with the aromatic amine should also be detected with the aliphatic amine, it is not possible to test this

hypothesis in these systems since no emission exciplexes are observed in compounds I(a) - IV(a).

Also the energy transfer mechanism would only be applicable to the aminoesters containing an aromatic amine since no energy transfer mechanism is possible between the aliphatic amine and the aromatic esters.

We are now studying the competition between energy transfer and electron transfer in these systems and a detailed kinetic study will be described in a forthcoming paper.

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