A comparative study of two exciplexes: anthracene-N,N-dimethylaniline and anthracene-julolidine systems

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Abstract

Two exciplex systems, anthracene-N,N-dimethylaniline and anthracene-julolidine, were studied. Although both N,N-dimethylaniline (DMA) and julolidine are aniline derivatives, they differ with regard to the twisting motion of the amino group. A comparative study of the effects of the donor concentration, medium polarity, temperature and magnetic field on the luminescence of the two exciplexes was performed. Differences in the behaviour of the two exciplexes were ascribed to differences in the structures of the two donors.

Keywords: Exciplex; Luminescence; Anthracene-N,N-dimethylaniline; Anthracene-julolidine; Magnetic field effect

1. Introduction

Extensive studies on exciplexes have been performed [1–5], but conformational aspects are still unknown [2–5]. When the intermolecular charge transfer (CT) excited state is lower in energy than the locally excited (LE) state, an exciplex may be formed. Coulombic interaction, appropriately screened by the medium, plays a dominant role in determining the mutual orientation of the partners of the exciplex [3–4]. Exciplexes between aromatic donors and aromatic acceptors presumably take up a sandwich configuration in order to maximize the overlap of the two charge clouds [4]. If, however, the donor and acceptor are linked by a flexible aliphatic chain, the geometry, to a considerable extent, is determined by the thermodynamics and dynamics of the chain folding process [5]. Another interesting observation in the case of the intramolecular CT state is that the donor group is frequently twisted out of the aromatic plane. For example, in p-N,N-dimethylaminobenzonitrile, the dimethylamino group twists itself out of plane of the aromatic ring [6]. Although this out-of-plane twisting of the dimethylamino group has been reported only when the acceptor group is chemically linked to the aromatic system, partial twisting of the dimethylamino group may occur even when the acceptor is not directly linked to the donor aromatic system. To throw light on this problem, we undertook a comparative study of the anthracene-N,N-dimethylaniline and anthracene-julolidine exciplexes, the rotation around the N–C bond being structurally prevented in the latter case. Detailed results of the exciplex luminescence of the anthracene-julolidine system as a function of the donor concentration, solvent polarity, temperature and magnetic field are reported.

2. Experimental details

2.1. Compounds

Anthracene was supplied by Aldrich Chemicals and was used as received. Julolidine was supplied by Aldrich Chemicals and was used after vacuum sublimation. N,N-Dimethylaniline (DMA) was supplied by BDH and was used after vacuum distillation.

2.2. Solvents

All the solvents were supplied by SD Chemicals. All were spectroscopic or high performance liquid chromatography (HPLC) grade and were used as supplied. Their purity was checked before use by measuring the background fluorescence. Traces of water were eliminated by adding anhydrous Na_2SO_4.

2.3. Spectra

Absorption spectra were determined on a JASCO UV-visible spectrometer (model-7850). Steady state emission and excitation spectra were recorded on a Perkin-Elmer

fluorescence spectrometer (MPF-44B). All solutions were degassed by nitrogen gas purging for 20 min. The temperature was controlled by a Neslab thermostat using water as heat carrier.

2.4. Fluorescence decays

Fluorescence decays were determined by a flash-lamp-operated, time-correlated single-photon-counting (TCSPC) unit. The apparatus has been described elsewhere [7]. Fluorescence decay curves were analysed by the deconvolution technique using a PTI global analysis program. The temperature was controlled by a Neslab thermostat using water as heat carrier.

2.5. Magnetic field effect

To determine the effect of a magnetic field on the exciplex luminescence, a phase-sensitive detection system was employed, the details of which have been discussed elsewhere [8]. The experiment was performed within a magnetic field range of 0–250 G at room temperature in tetrahydrofuran (THF), acetone and mixtures of these solvents in various proportions.

3. Results and discussion

3.1. Absorption and emission spectra

The absorption spectra of anthracene, julolidine, DMA, anthracene–julolidine and anthracene–DMA are shown in Figs. 1(a) and 1(b). The absorption and excitation spectra of anthracene–julolidine and anthracene–DMA resemble the sum of the spectra of the two chromophores. This suggests
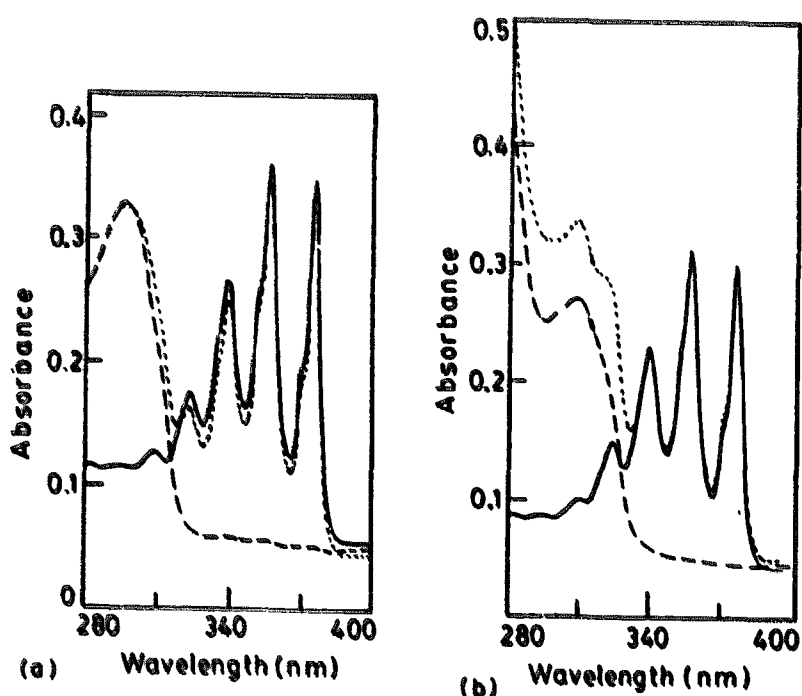

(a) Wavelength (nm) (b) Wavelength (nm)

Fig. 1. (a) Absorption spectra of anthracene (——), DMA (– – –) and anthracene–DMA (····) in cyclohexane at room temperature. (b) Absorption spectra of anthracene (——), julolidine (– – –) and anthracene–julolidine (····) in cyclohexane at room temperature.

that negligible interaction occurs between the chromophores in the ground state. The corresponding representative emission bands are shown in Figs. 2(a) and 2(b) for the two systems. The luminescence properties are discussed below.

3.2. Effect of donor concentration on exciplex luminescence at room temperature

As expected, with an increase in julolidine or DMA (donor) concentration (10^{-2} M), the intensity of the anthracene (acceptor) (10^{-4} M) emission band gradually decreases and the intensity of the exciplex band simultaneously increases. When we plot the ratio of the intensity of unquenched to quenched anthracene emission I_A^0/I_A at 405 nm against the julolidine concentration, the plot (Fig. 3(a)) shows positive curvature which fits a second-order polynomial where the coefficients of the first-order and second-order terms are 59 and 1184 respectively in cyclohexane, and 63 and 3725 respectively in ethyl acetate. On the other hand, for the anthracene–DMA system, I_A^0/I_A at 405 nm varies almost linearly with the DMA concentration (Fig. 3(a)) with slopes of 34 and 84 in cyclohexane and ethyl acetate respectively. The ratio of the peak intensity of the exciplex emission to the anthracene emission I_E/I_A also varies linearly with the donor concentration for both systems (Fig. 3(b)).
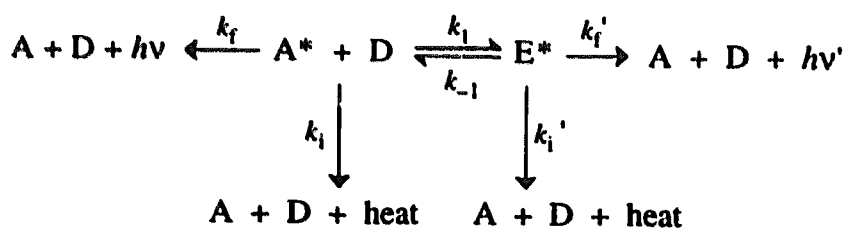
The nature of the curves for I_A^0/I_A vs. donor concentration and I_E/I_A vs. donor concentration may be discussed within the framework of a simple exciplex formation scheme (Scheme 1) where k_f and k_f' are the radiative decay rate constants of the acceptor (anthracene) and the exciplex respectively, k_i and k_i' are the corresponding non-radiative decay rate constants and k_1 and k_{-1} are the rate constants of the exciplex formation and dissociation processes respectively. Considering the above reaction scheme, the deduced expressions of I_A^0/I_A and I_E/I_A are

$$I_A^0/I_A = 1 + \frac{k_q[D]}{k_i + k_f}$$

$$= 1 + \tau_A^0 k_q[D] = 1 + k_{SV}[D] \tag{1}$$

where

$$\tau_A^0 = k_f + k_i$$

and

$$A + D + h\nu \xleftarrow{\;k_f\;} A^* + D \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E^* \xrightarrow{\;k_f'\;} A + D + h\nu'$$

$$\downarrow{k_i} \qquad\qquad \downarrow{k_i'}$$

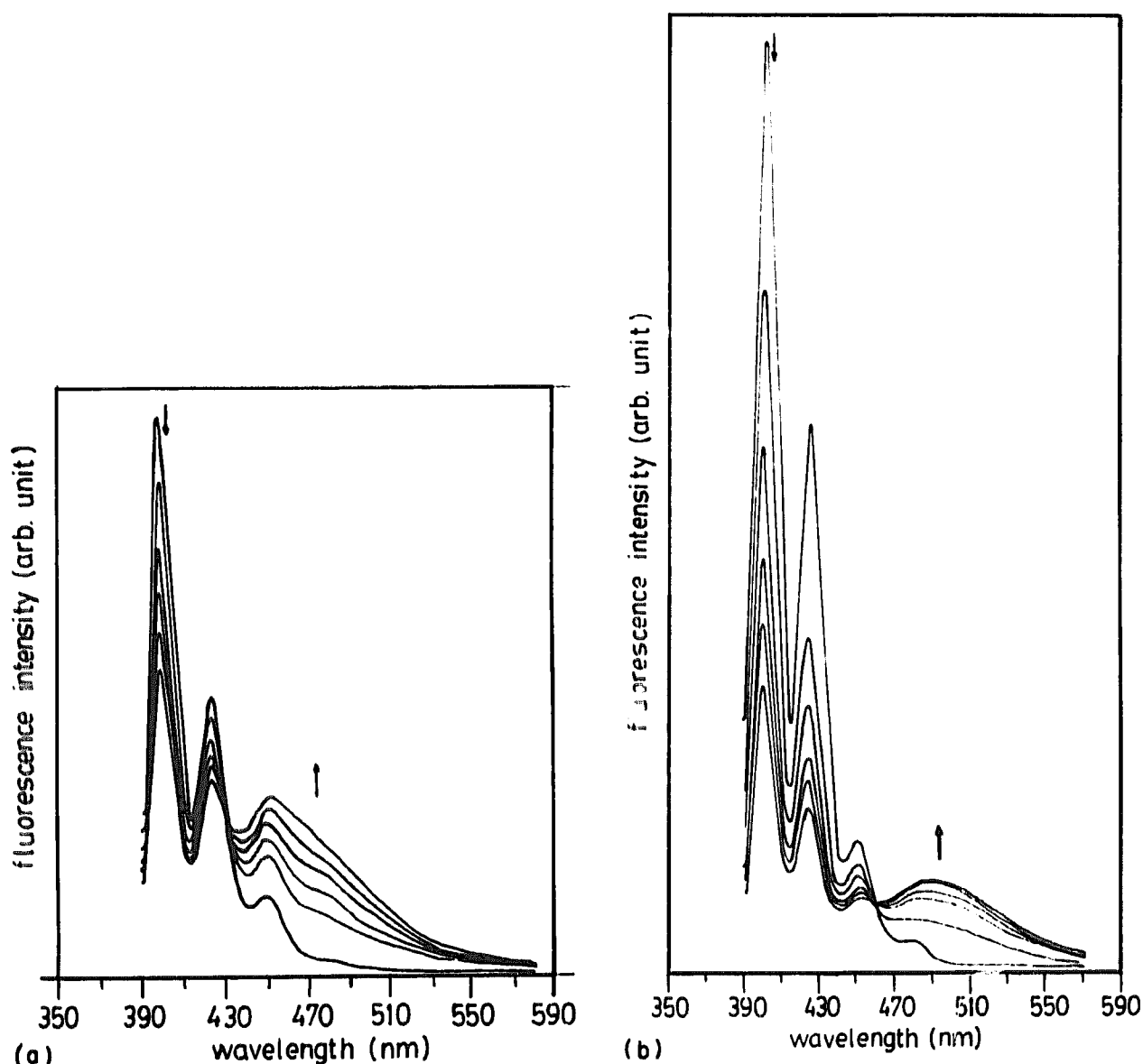$$A + D + heat \qquad A + D + heat$$

Scheme 1.

Fig. 2. (a) Fluorescence spectra of the anthracene–DMA system in cyclohexane. The excitation wavelength is 377 nm. The direction ᴐf the arrows indicates the trend of the emission intensity change with increasing DMA concentration. (b) Fluorescence spectra of the anthracene–julolidine system in cyclohexane. The excitation wavelength is 377 nm. The direction of the arrows indicates the trend of the emission intensity change with increasing julolidine concentration.

$$k_{SV} = \tau_A{}^0 k_q$$

$$k_q = k_1\left(1 + \frac{k_{-1}}{k'_f + k'_i}\right)^{-1} = pk_1$$

$$p = \left(1 + \frac{k_{-1}}{k'_f + k'_i}\right)^{-1}$$

$$I_E/I_A = \frac{k'_f k_1 [D]}{k_f(k'_f + k'_i + k_{-1})} \qquad (2)$$

Eq. (1), known as the Stern–Volmer equation, predicts a linear relationship between $I_A{}^0/I_A$ and the donor concentration, if k_q is truly a constant. This is observed for anthracene–DMA, but not for anthracene–julolidine where a positive deviation occurs. What could be the possible reason for the positive deviation from the Stern–Volmer plot in the case of
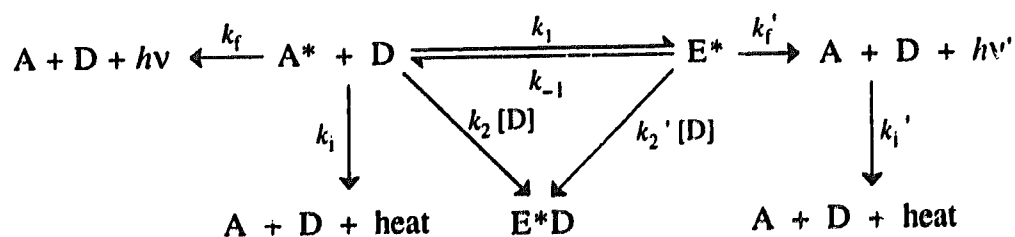
anthracene–julolidine? One explanation could be the formation of a triplex which does not fluoresce in the region of exciplex fluorescence. The scheme could be depicted as shown in Scheme 2.

Assuming steady state conditions, this leads to the following expressions for $I_A{}^0/I_A$ and I_E/I_A

$$I_A{}^0/I_A = 1 + k_1 gt_A{}^0[D] + k_2\tau_A{}^0[D]^2 \qquad (3)$$

$$I_E/I_A = \frac{k'_f k_1 [D]}{k_f(k'_f + k'_i + k_{-1} + k'_2[D])} \qquad (4)$$

Thus we expect a positive deviation from linearity in the case of $I_A{}^0/I_A$, but a negative deviation in the case of I_E/I_A. The experimental curvature agrees for $I_A{}^0/I_A$ vs. donor concentration, but not for the corresponding I_E/I_A plot.
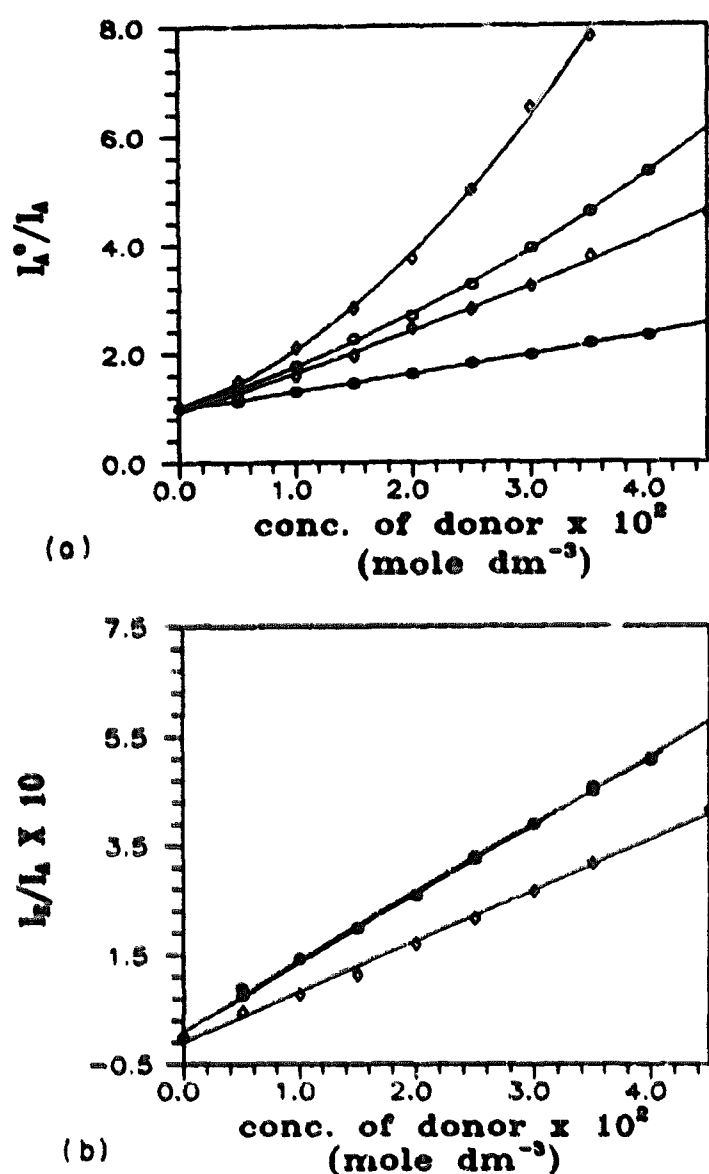

Scheme 2.

$$k = \frac{4}{3} \pi r_q^3 N \qquad (5b)$$

where r_q is the radius of the active sphere and N' is the number of donor molecules per millimole of the compound. Eq. (5a) predicts a positive deviation from linearity for the Stern–Volmer plot, as observed.

A similar explanation of positive deviation was offered by Noyes [13] and Weller [14]. Using the Smoluchowski equation for a diffusion-controlled quenching process, Weller [14] found that the diffusion rate constant k_{diff} contains a transient term

$$k_{diff} = 4\pi N' r_q(\mathscr{D}_A + \mathscr{D}_D) + 4r_q^2[\pi(\mathscr{D}_A + \mathscr{D}_D)/t]^{1/2} \qquad (6)$$

where r_q is the radius of the reaction sphere and $\mathscr{D}_A$ and $\mathscr{D}_D$ are the diffusion coefficients of the acceptor and donor respectively. Due to the presence of the transient term in the expression of the diffusion rate constant, the Stern–Volmer equation under certain approximations is modified to the following form

$$I_A^0/I_A = (1 + k_q r_A^0[D]) \exp[V_D(I_A/I_A^0)^{1/2}[D]] \qquad (7a)$$

$$V_D = 4\pi N' r_q^2[(\mathscr{D}_A + \mathscr{D}_D)\tau_A^0] \qquad (7b)$$

$$k_q = 4\pi N' r_q(\mathscr{D}_A + \mathscr{D}_D) \qquad (7c)$$

Therefore due to the dependence of k_q and V_D on the donor concentration [D], I_A^0/I_A will vary non-linearly with the donor concentration. Our data cannot differentiate between the last two mechanisms which are conceptually similar.

On the basis of the last two mechanisms, we offer some possible reasons for the positive deviation in the Stern–Volmer plot for the julolidine complex compared with the zero deviation for the DMA complex. In julolidine, the N atom is rigidly fixed by the two chains, so that the N lone pair can easily conjugate with the π orbitals of the ring. The DMA group is twisted in the S_1 state in both unsubstituted [15] and acceptor-group-substituted [16] DMA. Thus we expect the ionization potential (in the S_1 state) of julolidine to be smaller than that of DMA. This will make the quenching radius r_q larger for julolidine, since the distance through which the electron can jump has been shown to be greater for a good donor than for a bad donor [17]. Assuming a quenching probability p equal to unity, the quenching rate constant and quenching radius can be calculated using Eq. (7) and are shown in Table 1. These estimated values indicate that the electron transfer distance is smaller for non-polar solvents

Fig. 3. (a) Variation of the acceptor fluorescence intensity ratio I_A^0/I_A with the donor concentration for the anthracene–DMA system in cyclohexane (●) and ethyl acetate (♦) and for the anthracene–julolidine system in cyclohexane (○) and ethyl acetate (◇). (b) Variation of the ratio of the emission intensity of the exciplex to that of the locally excited state for the anthracene–DMA system in cyclohexane (●) and ethyl acetate (♦) and for the anthracene–julolidine system in cyclohexane (○).

Another explanation might be offered on the basis of the multiplicity of the fluorescent state [9]. However, the lifetimes and band shapes do not provide any evidence for this in the present case. The non-linearity of the Stern–Volmer plot could also arise due to the presence of a static active sphere around the fluorophore [10]. Let us suppose that there is an active sphere around the excited anthracene molecule, and the presence of one or more donor molecules within the active sphere leads to the rapid deactivation of anthracene at the moment of anthracene excitation. A certain fraction of anthracene would decay extremely rapidly and would be unlikely to fluoresce (in the wavelength range of anthracene); the remaining fraction of anthracene would form an exciplex with a slower rate constant. The fraction of anthracene which is not immediately quenched would be proportional to $\exp(-\lambda)$, where λ is the average number of donor molecules within the active volume [11] and, hence, proportional to [D]. Then I_A^0/I_A is given by the following expression [12]

$$I_A^0/I_A = (1 + k_{SV}[D]) \exp(\lambda)$$
$$= (1 + k_{SV}[D]) \exp(k[D]) \qquad (5a)$$

Table 1
Quenching rates and quenching radius of the exciplexes in different solvents

Solvent	Anthracene–DMA		Anthracene–julolidine	
	k_q (s^{-1} mol^{-1})	r_q (Å)	k_q (s^{-1} mol^{-1})	r_q (Å)
Cyclohexane	2.4×10^9	–	5.4×10^9	7.7
Ethyl acetate	5.7×10^9	–	8.0×10^9	11.9

than for polar solvents. This explains the increased curvature for more polar solvents (Fig. 3(a)). It is probable that contact ion pairs (CIP) are directly formed in the case of non-polar solvents, while more solvent-shared ion pairs (SSIP) are generated directly in comparatively polar solvents.

3.3. Effect of polarity on exciplex emission at room temperature

Anthracene–julolidine and anthracene–DMA exciplex emissions were studied in several solvents (cyclohexane, benzene, diethyl ether, ethyl acetate, THF and dichloroethane). With an increase in solvent polarity, the exciplex emission band becomes less intense, broader and more red shifted.

In any particular solvent (even in cyclohexane), the intensity of the anthracene–julolidine exciplex fluorescence is less than that of the anthracene–DMA exciplex. It is also found that the relative change in the exciplex intensity with polarity is greater than the relative change in the exciplex decay rate (discussed in Section 3.5). The latter observation indicates the presence of channels other than exciplex formation for the process of anthracene fluorescence quenching by electron donors. In a polar solvent, the emissive exciplex formation rate competes with the solvent-separated iron pair formation rate and the triplet formation (intersystem crossing (ISC)) rate [18]. The last two processes are apparently faster for the anthracene–julolidine system than the anthracene–DMA system; as a result, the intensity of the anthracene–julolidine exciplex is less than that of the anthracene–DMA exciplex in any solvent. This is consistent with the effect of the magnetic field on the exciplex luminescence (discussed in Section 3.6).

In polar solvents, the bathochromic shift of the exciplex emission is expected to depend linearly on the solvent parameter $f(\epsilon, n)$.

$$\bar{\nu}_{f0} - \bar{\nu}_f = \frac{2(\mu_c - \mu_g)^2}{4\pi\epsilon_0 hc\rho^3} f(\epsilon, n) \quad (8a)$$

where

$$f(\epsilon, n) = \frac{\epsilon - 1}{2\epsilon - 1} - \frac{n^2 - 1}{2(2n^2 - 1)} \quad (8b)$$

$\bar{\nu}_f$ and $\bar{\nu}_{f0}$ are the emission peak wavenumbers in a solvent with dielectric constant ϵ and refractive index n and in vacuum respectively; ϵ_0, h, c and ρ correspond to the permittivity of vacuum (8.85×10^{-12} C V^{-1} m^{-1}), Planck's constant (6.625×10^{-34} J s), the velocity of light (3×10^8 m s^{-1}) and the radius of the cavity (in metres) respectively; μ_c and μ_g are the permanent dipole moments (C m) of the excited and ground states of the exciplex respectively. For the anthracene–julolidine system, the slope of the linear curve is 20 857 cm^{-1} (Fig. 4(a)). Assuming 4.8 Å for ρ and 1.5 D (5×10^{-30} C m) for μ_g, the excited state dipole moment μ_c of the exciplex is calculated to be 15 D (50.0×10^{-30} C m).
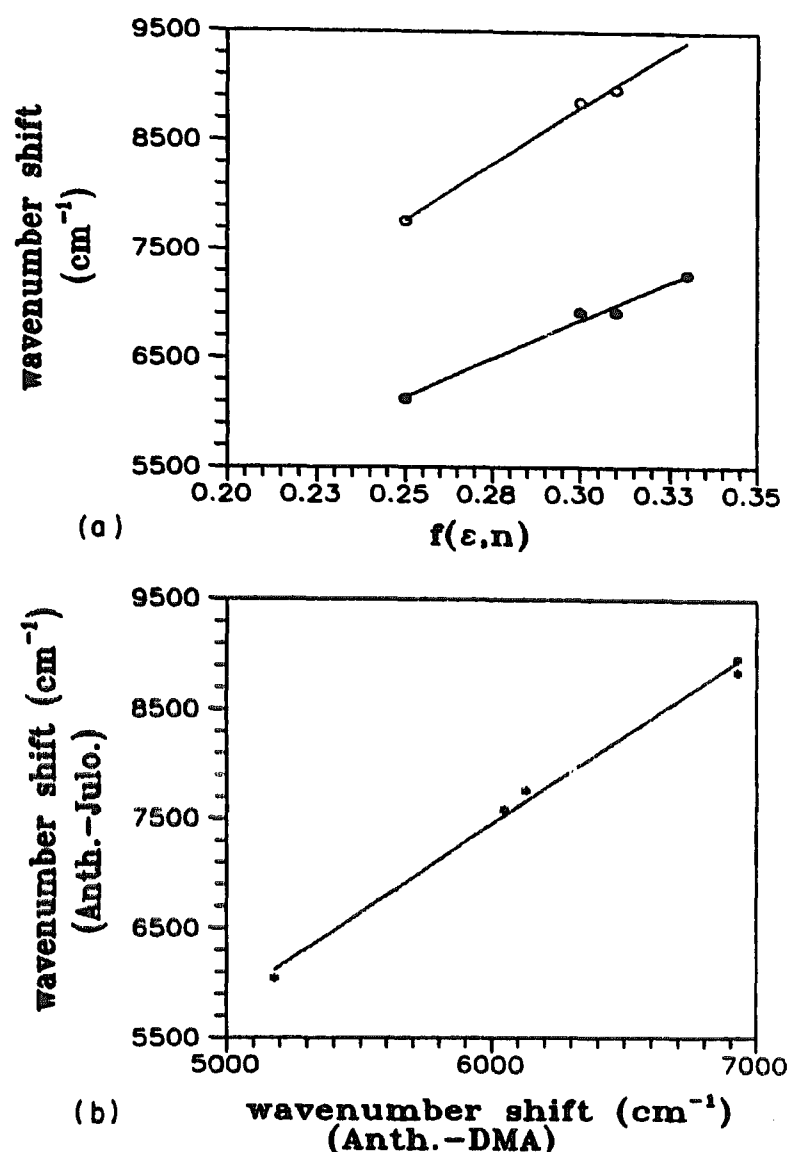

Fig. 4. (a) Lippert–Mataga plots (see text) for anthracene–DMA (●) and anthracene–julolidine (○) systems in polar solvents. (b) Wavenumber shift ($\bar{\nu}_{f0} - \bar{\nu}_f$) of the exciplex emission intensity due to dielectric constant variation for the anthracene–julolidine system relative to that for the anthracene–DMA system. $\bar{\nu}_{f0}$ and $\bar{\nu}_f$ are the wavenumbers corresponding to the exciplex emission intensity maximum in vacuum and in a solvent of dielectric constant ϵ and refractive index n.

In comparison, the slope of the linear curve of the anthracene–DMA exciplex is 14 184 cm^{-1} corresponding to 12.5 D for μ_c. We therefore conclude that the degree of charge transfer is larger in the anthracene–julolidine exciplex. It may be pointed out that deviations from the Lippert–Mataga plot are frequently observed in non-polar solvents due to the intramolecular rearrangement of the exciplex [19], and this case is no exception. We have therefore plotted the bathochromic shift of the anthracene–julolidine emission band maxima vs. that of the anthracene–DMA exciplex; this is found to be linear for all solvents (Fig. 4(b)).

The relatively larger dipole moment of the anthracene–julolidine complex is consistent with its relatively larger Stokes shift (i.e. $\nu_{absorbance} - \nu_{emission}$). The Stokes shift observed cannot be due to the conformational rearrangement of the donor, since in that case it would have been larger for the more flexible DMA. This shift presumably arises from solvent reorganization, the energy of which is larger for the julolidine complex than the DMA complex because of the relatively larger dipole moment of the julolidine complex.

It has been shown that the exciplex bandwidth depends on the outer-sphere reorganization energy [20], and theoretically the two are related by the expression

$$(\Delta \nu)^2 / (8 \ln 2) = 2\lambda_{out} kT + 2\lambda_{int} kt + \lambda_{inh} h\nu_{inh} \qquad (9a)$$

where λ_{int} is the intramolecular reorganization energy associated with vibrations for which $h\nu_{int} < kT$, λ_{inh} is the intramolecular reorganization energy associated with vibrations for which $h\nu_{inh} > kT$ and λ_{out} is the outer-sphere solvent reorganization energy for the transition from the excited state with dipole moment μ_e to the ground state with dipole moment μ_g; it is given by the expression

$$\lambda_{out} = \frac{(\mu_e - \mu_g)^2}{4\pi\epsilon_0\rho^3} \left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1} \right) \qquad (9b)$$

Since the anthracene–julolidine exciplex has a higher dipole moment, its bandwidth should be larger than that of the anthracene–DMA exciplex, as is observed experimentally. This explanation of the bandwidth of the exciplex luminescence should be regarded as tentative and needs to be substantiated by studies on other similar pairs of donors and acceptors.

3.4. Effect of temperature on the steady state exciplex emission

The steady state spectra of anthracene–julolidine and anthracene–DMA systems were studied at various temperatures in the range 5–70 °C. The ratio of the anthracene–julolidine exciplex band intensity I_E to that of the LE state I_A increases with an increase in temperature in all solvents. For the anthracene–DMA system, the intensity ratio decreases with temperature in cyclohexane, but increases with temperature up to 60 °C in benzene and then decreases; in other polar solvents (ethyl acetate, THF), this ratio increases with increasing temperature within our experimental temperature range. The plots of I_E/I_A vs. $1/T$ are shown in Figs. 5(a) and 5(b).

The excited state potential energy curve appropriate for non-polar solvents is shown schematically in Fig. 6 [21]. The energy of the zero-order ionic state (D^+A^-) at infinite separation is expected to be greater than that of the non-ionic zero-order LE state (DA^*). However, at short distances, its energy decreases due to coulombic interaction, while that of the zero-order LE state (DA^*) increases due to repulsion; the curves cross leading to a lower excited state which is ionic at short distances and non-ionic at large distances. The schematic diagram in Fig. 6 is consistent with the exciplex reaction kinetics shown in Scheme 1, which lead to Eq. (2). If we assume that k_f, k'_f and k'_i are temperature independent, but k_1 and k_{-1} obey the Arrhenius rate law [22], we obtain the following expression for the temperature dependence of I_A / I_E

$$I_A / I_E = \frac{k_f \exp(E_1 / RT)}{k'_f [[D] k_1^0}$$

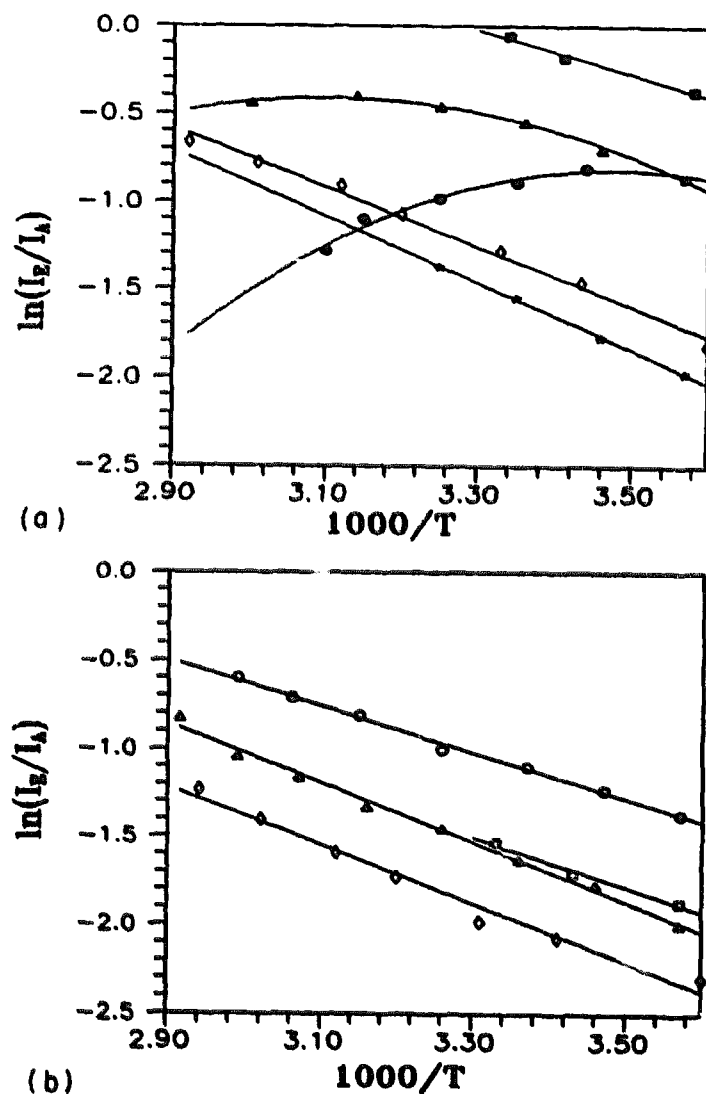$$\times [(k'_f + k'_i) + k_{-1}^0 \exp(-E_{-1} / RT)] \qquad (10)$$

Fig. 5. (a) Influence of temperature on the ratio of the emission of the exciplex to that of the LE state for the anthracene–DMA system in several solvents: ●, cyclohexane; ▲, benzene; ■, diethyl ether; △, ethyl acetate; *, THF. (b) Influence of temperature on the ratio of the emission intensity of the exciplex to that of the LE state for the anthracene–julolidine system in several solvents: ○, cyclohexane; △, benzene; □, diethyl ether; ◇, ethyl acetate.
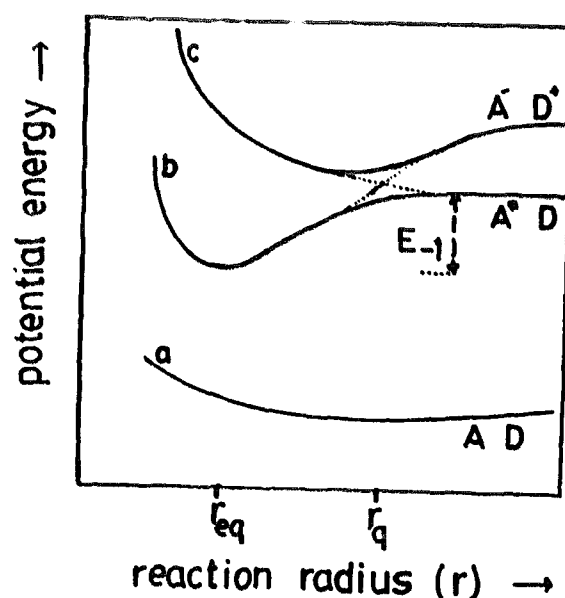

Fig. 6. Schematic potential energy curves in non-polar solvents: r_q is the effective quenching radius and r_{eq} is the equilibrium distance between the donor and the acceptor within the exciplex. The curves (a), (b) and (c) represent the ground state, charge transfer state (exciplex) and the donor–acceptor repulsive state (LE).

Table 2
The exciplex formation activation energy [a] in different solvents

Solvent	E_v (kJ mol^{-1})	E_i or ΔE (kJ mol^{-1})	
		Anthracene–DMA	Anthracene–julolidine
Cyclohexane	12.8	– 10.7	11.2
Benzene	14.1	–	10.4
Diethyl ether	5.3	10.0	11.6
Ethyl acetate	8.4	14.1	13.8
THF	9.5	15.6	–

[a] For the anthracene–DMA system in cyclohexane, the negative sign indicates the exciplex stabilization energy.

where E_1 and E_{-1} are the exciplex formation and dissociation activation energies respectively. The exponential term outside the bracket should cause a decrease in I_A/I_E with temperature; on the other hand, the expression within the bracket should increase I_A/I_E. In the limit $(k'_f + k'_i) \gg k_{-1}^0 \exp(-E_{-1}/RT)$, a negative slope for $\ln(I_E/I_A)$ vs. $1/T$ will be observed. This means that the dissociation rate of the exciplex is small compared with its radiative and non-radiative decay rates to the ground state; thus, even though the dissociation rate is temperature dependent, the overall decay rate of the exciplex is only decreased slightly by temperature; the formation rate (mostly diffusion controlled) of the exciplex, which increases with temperature, is the deciding factor in determining I_E/I_A. If, however, $(k'_f + k'_i) \ll k_{-1}^0 \exp(-E_{-1}/RT)$, the slope of the plot of $\ln(I_E/I_A)$ vs. $1/T$ will be positive, as E_{-1} is expected to be greater than E_1. This limit corresponds to a quasi-equilibrium between A^* and DA^*. Which of the two situations prevails depends on the values of E_{-1} (which is approximately equal to the exciplex stabilization energy), k_{-1}^0 and $k'_f + k'_i$. Assuming that k_{-1}^0 s the same for both exciplexes, both $k'_f + k'_i$ and E_{-1} must be larger for the julolidine complex than for the DMA complex; the first is inferred from exciplex lifetime measurements (see later) and the second from exciplex emission frequency measurements and ionization energy estimation as discussed earlier. Thus, for the julolidine complex, a $\ln(I_E/I_A)$ vs. $1/T$ plot in cyclohexane gives a negative slope, while the reverse is true for the DMA complex. The activation energy of the exciplex formation process was estimated for the first case; the estimated value is close to the solvent viscosity activation energy (see Table 2), as expected for a diffusion-controlled process. In the second case (i.e. DMA complex), we can estimate the exciplex stabilization energy from the slope of the tangent of the $\ln(I_E/I_A)$ vs. $1/T$ curve at the higher temperature limit. It is 22 kJ mol^{-1}, which is small compared with the value (8.4 kcal mol^{-1}) estimated by others [23]. This discrepancy indicates that, although the $\ln(I_E/I_A)$ vs. $1/T$ curve shows a positive slope with negative curvature within our experimental temperature range, it is still far from the high temperature limiting value, and as such it is not possible to determine the true binding energy of the exciplex from this experimental curve.

In a slightly polar solvent such as ether, or non-polar but polarizable solvent such as benzene, the above schematic diagram may still be considered valid. However, the solvent should lower the energy of the zero-order D^+A^- curve with respect to the DA^* curve. Thus an increase in E_{-1} is expected; this should cause an increase in $(k'_f + k'_i)$ compared with $k_{-1}^0 \exp(-E_{-1}/RT)$ and, in some cases, may cause a reversal of the positive slope to a negative one. This is observed for the anthracene–DMA complex; the slope is indeed negative for all slightly polar solvents. For benzene, the plot goes through a maximum (Fig. 5(a)). The activation energy for exciplex formation (E_1) has been estimated for all cases of positive slope, and is given in Table 2. It should be noted that, in these solvents, the measured activation energies are greater than the activation energy for viscosity of the corresponding solvent. The fact that, in polar solvents, the activation energy of exciplex formation exceeds the activation energy for solvent viscosity supports the model which assumes the direct formation of an SSIP instead of a CIP (exciplex) in these solvents.

It is worth noting here that an increase in exciplex intensity with temperature has been observed by others for cases in which the donor and acceptor moieties are joined by spacers [4]. To explain the increase in I_E with temperature of some intramolecular amine–benzene exciplexes, der Auweraer et al. [4] proposed that a rise in temperature increases the amplitude of vibration of the two components of the exciplex, and thus increases the time average transition moment of the exciplex emission; this leads to an increase in k'_f, and as a result, the exciplex fluorescence yield increases. This argument is based on an assumed high symmetry of the complex. In our case, the overall symmetry of the acceptor or donor is low and the nodal planes of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the donors and acceptors are too extensive; hence the change in the transition moment of the exciplex emission due to the increase in thermal vibration is assumed to be small.

3.5. Effect of temperature on the transient exciplex emission

For non-polar solvents, the kinetics of exciplex emission can be discussed within the framework of the previously given scheme. For simplicity, we first assume the absence of an active sphere around the excited anthracene moieties. For δ-pulse excitation, the transient LE state decay $(I_A(t))$ and the exciplex decay $(I_E(t))$ are described by the equations

$$I_A(t) = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} \tag{11a}$$

$$I_E(t) = C_3(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \tag{11b}$$

where

$$C_2/C_1 = (X - \lambda_1)/(\lambda_2 - X) \qquad (12a)$$

$$C_3 = k_1 [A^*][D]/(\lambda_2 - \lambda_1) \qquad (12b)$$

$$\lambda_{2,1} = 0.5\{(X + Y) \pm [(X - Y)^2 + 4k_1 k_{-1}[D]]^{1/2}\} \qquad (12c)$$

$$X = k_f + k_i + k_1[D] \quad Y = k'_f + k'_i + k_{-1} \qquad (12d)$$

Thus the acceptor decays exponentially with two different decays constants; the pre-exponential factors are also different. The exciplex luminescence time variation is expressed as the sum of two parts with the same two rate constants, one for growth and the other for decay, and the pre-exponential factors are equal.

In the presence of a static active sphere, Eqs. (11) and (12) are not correct, because the initial conditions, at $t = 0$, $[E] = 0$ and $[A^*] = [A^*]_0$, are no longer valid. In the presence of a static active sphere, the temporal behaviour of the exciplex luminescence should consist of three parts, one for decay and two for growth. If a fraction of the acceptor forms an exciplex at a very fast rate with the donor molecule present within the static active sphere, and the rate is beyond our experimentally measurable limit, then the boundary condition should be chosen as $t = 0$, $[E] = [E]_0$ rather than $[E] = 0$. As a consequence, the coefficient of growth (C_{3g}) and the coefficient of decay (C_{3d}) will not be the same. The deviation of the ratio C_{3g} to C_{3d} from unity should increase with increasing radius of the active sphere. For the same reason, in the double exponential fit of the exciplex transient emission, the apparent λ_2 values determined from the acceptor emission and the exciplex growth will be different.

In cyclohexane, the exciplex emission of both DMA and julolidine shows a rapid growth followed by decay. However, for the DMA complex, the two pre-exponential terms are almost equal; this is not observed for the julolidine complex. Secondly, λ_1 and λ_2 determined from exciplex emission and anthracene decay are nearly the same for the DMA complex. For the julolidine complex, the coefficient C_1 of anthracene decay is so small that λ_1 cannot be determined; the λ_2 values determined from anthracene decay and exciplex growth are also somewhat different. All these observations point to the existence of a large static active sphere for the julolidine complex, a conclusion consistent with our steady state concentration quenching studies (Section 3.2). The observation that C_1/C_2, determined from anthracene decay for the anthracene–julolidine system, is small implies that k_{-1} is small (see Eq. (12)) for the julolidine complex. This is consistent with our assumption that $k'_f + k'_i \gg k_{-1}$ in Section 3.4.

In polar solvents, even the DMA complex exhibits deviation from the expectations of the simple model. For both the DMA and julolidine complexes, the difference between C_2 and C_1 in exciplex emission increases with the polarity of the medium. This can be ascribed partly to the enlargement of the static active sphere with polarity and partly to ion formation in polar solvents.

We have studied the effect of temperature on time-resolved curves. Plots of $\ln \lambda_2$ and $\ln \lambda_1$ as a function of $1/T$ are shown
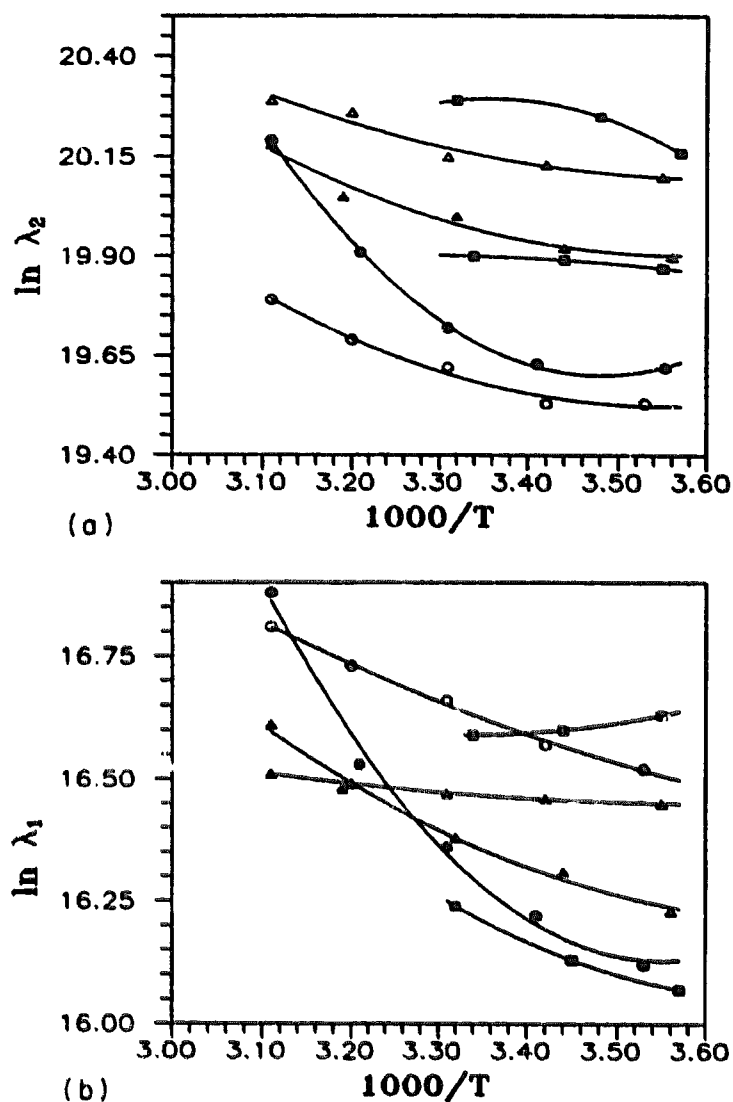

Fig. 7. (a) Influence of temperature on $\ln \lambda_2$ of the anthracene–DMA system in cyclohexane (●), benzene (▲) and diethyl ether (■), and of the anthracene–julolidine system in cyclohexane (○), benzene (△) and diethyl ether (□). (b) Influence of temperature on $\ln \lambda_1$ of the anthracene–DMA system in cyclohexane (●), benzene (▲) and diethyl ether (■), and of the anthracene–julolidine system in cyclohexane (○), benzene (△) and diethyl ether (□).

in Figs. 7(a) and 7(b). It is observed that, in cyclohexane, the decrease in λ_2 with an increase in temperature is much faster for the DMA complex than for the julolidine complex. Since the lifetime of the exciplex is $1/(k'_f + k'_i + k_{-1})$ and only k_{-1} is expected to increase with temperature, the ratio $k_{-1}/(k'_f + k'_i)$ will be smaller for the julolidine complex than for the DMA complex. This is consistent with our explanation of the anomalous temperature dependence of the steady state emission of the julolidine–anthracene exciplex (Section 3.4). In slightly polar solvents, the curve becomes less steep for both julolidine and DMA complexes. As explained earlier, in polar solvents an increase in E_{-1} is expected. This makes k_{-1} ($= k_{-1}^0 \exp(-E_{-1}/RT)$) smaller compared with $k'_f + k'_i$ leading to a smaller temperature variation of λ_2.

3.6. Effect of magnetic field on exciplex luminescence

In previous paragraphs, it has been noted that, with an increase in the solvent polarity, the SSIP yield increases. The initially formed singlet "solvent-shared" radical pairs may recombine directly within a few nanoseconds or after a round-trip diffusional excursion process which may take a few

microseconds [18a,24,25]. During the diffusional excursion process, non-reversible loss due to triplet radical pair formation by the ISC process or due to interpair recombination may occur [18a,25]. A decrease in the triplet formation yield on application of a magnetic field causes an increase in the CIP (i.e. emissive exciplex) yield. It has been shown [26] that hyperfine interaction (HFI) in unpaired radicals plays an important role in this process of spin multiplicity change. A weak external magnetic field decreases the HFI-controlled $(S, T_0) \leftrightarrow T_{\pm 1}$ probability, and hence increases the exciplex fluorescence yield. The exciplex magnetic field effect becomes saturated when the Zeeman separation is large enough to reduce the HFI-induced $(S, T_0) \leftrightarrow T_{\pm 1}$ transition probability almost to zero. The field $(B_{1/2})$ at which the magnetic-field-induced change is half of the value at saturation is considered to be a rough measure of the extent of HFI present in the two radicals [27].

Plots of the normalized-field-induced change of the exciplex luminescence intensity vs. magnetic field are shown in Figs. 8(a) and 8(b). The measured $B_{1/2}$ value in both cases is around 73 G. This shows that HFIs in both exciplexes, anthracene–DMA and anthracene–julolidine, are of the same order. However, the percentage magnetic field effect (i.e $(\Delta\phi/\phi) \times 100$, where $\Delta\phi$ is the field-induced change in the fluorescence yield ϕ) in polar solvents (or solvent mixtures) is very different in the two cases. Fig. 9 shows $\Delta\phi/\phi$ for solvent mixtures of different dielectric constant. Although
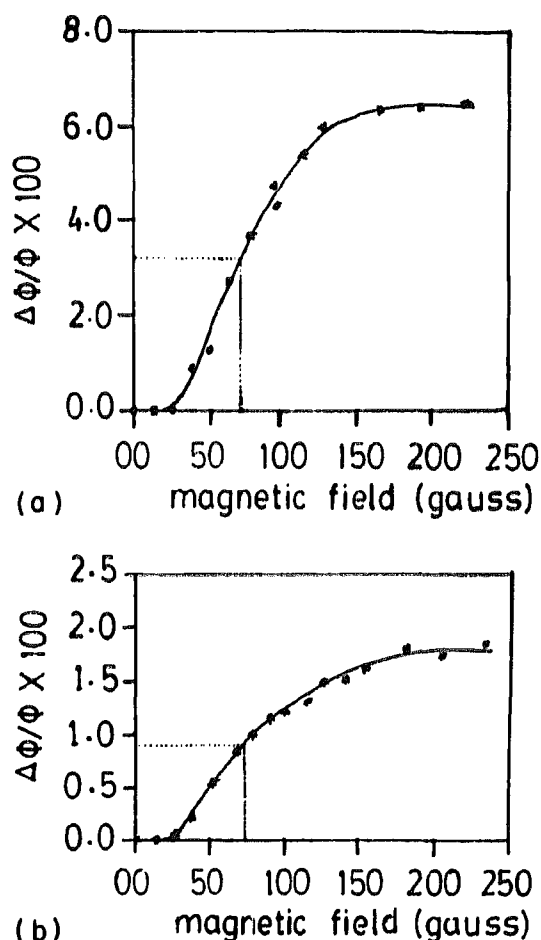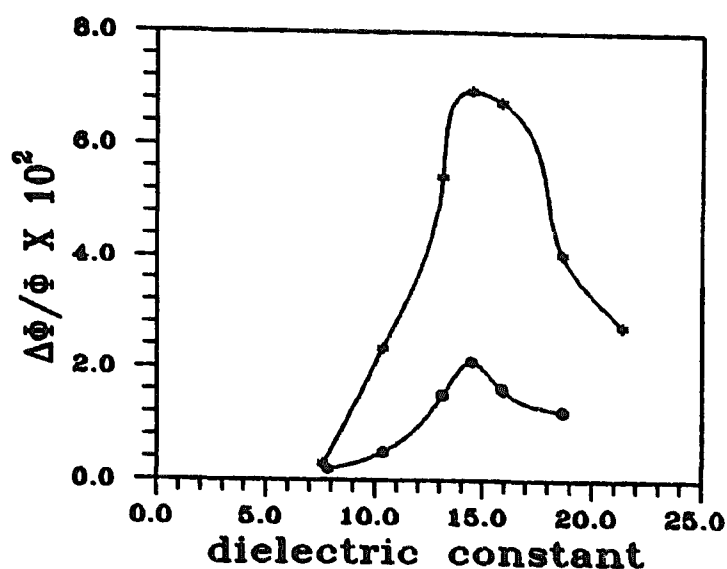

Fig. 9. Variation of the magnetic-field-modulated luminescence ratio ($\Delta\phi/\phi$) of the anthracene–DMA system (*) and anthracene–julolidine system (●) at 560 nm and 640 nm respectively as a function of the dielectric constant (ϵ) of the medium: ϵ was varied using THF–acetone mixtures of different proportions.

the shapes of the two curves are similar, one is three times the height of the other at the maximum of the curve. Naturally, the HFI (as measured by $B_{1/2}$) cannot explain this difference. The field-free spatial diffusion rates of the DMA$^+$ and julolidine$^+$ radicals are expected to be the same and so a difference in the diffusion coefficients can also be ruled out as the probable cause. The distance between the partners of the radical pairs at the time of generation is expected to be greater for anthracene–julolidine than for anthracene–DMA, because the julolidine molecule has a lower ionization potential and hence a larger radius of capture (see Section 3.2). This may explain why ϕ for the julolidine complex is less than that for the DMA complex, but not why $\Delta\phi/\phi$ is much smaller for the julolidine complex. Similarly, any reasonable assumption regarding the barrier between the SSIP and CIP runs into difficulty and cannot account for the fact that both ϕ and $\Delta\phi/\phi$ are less for the julolidine complex than for the DMA complex in the solvent mixtures. A combination of the factors mentioned above may explain the observation. It is probable that a small percentage of the magnetic field effect may arise from the shorter lifetime (as measured by us) of the julolidine complex. This shorter lifetime does not permit long diffusive excursions of the radical pairs, which is necessary for the observation of a magnetic field effect on the relatively slow $S \leftrightarrow T$ rephasing process. It may also be that the recombination radius of the radical pairs is different in the two cases (for the same reason for which the capture radius is different). It may also be necessary to explore the possibility of internal rotations, such as that of the CH_3 group or $(CH_3)N$ group, being coupled with spin motion, thereby increasing the ISC rate. However, we feel that at the present juncture our knowledge is insufficient to make a choice from the possible alternatives.

4. Conclusions

Julolidine–anthracene and DMA–anthracene exciplexes, despite their structural similarities, exhibit marked differ-

Fig. 8. (a) Dependence of the magnetic-field-modulated luminescence ($\Delta\phi$) on the magnetic field for the anthracene–DMA exciplex in a THF–acetone mixture ($\epsilon = 14.5$) at 560 nm. (b) Dependence of the magnetic-field-modulated luminescence ($\Delta\phi$) on the magnetic field for the anthracene–julolidine exciplex in a THF–acetone mixture ($\epsilon = 14.5$) at 640 nm.

ences in terms of the dependence of the exciplex emission on the concentration of the donor, medium polarity, temperature, lifetime and magnetic field. Most of the differences can ultimately be traced to structural differences between the two donors, which are responsible for different conjugation of the N lone pair with the phenyl ring. In order to understand the magnetic field effect, however, further investigations are necessary.

Acknowledgements

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