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Investigations of excited state quenching reactions between *p*-toluidine, its *N*,*N*-dimethyl derivative and the acceptor dimethylterephthalate at different temperatures

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Abstract

Electronic absorption and steady state and time-resolved emission spectroscopy were used to investigate the occurrence of several non-radiative processes, e.g. excitational energy transfer, photoinduced electron transfer, etc., between the electron donors *p*-toluidine (p-tol) and its *N*,*N*-dimethyl derivative (N,N-DM-p-tol) and the well-known acceptor dimethylterephthalate (DMTP) in solvents of different polarity at 296 K and in ethanol (EtOH) rigid glassy matrix at 77 K. From the room temperature experimental results, the strong dynamic fluorescence quenching phenomena observed for the toluidine donors in the presence of the acceptor DMTP may be due mainly to the combined effect of two non-radiative processes: (1) photoinduced electron transfer from the excited (S_1) donor to the ground state acceptor; (2) enhanced intersystem crossing (isc) within the donor as the S_1 state acquires $n\pi^*$ character due to conformational changes in the presence of DMTP. Lack of spectral overlap between the donor emission and acceptor absorption excludes the possibility of the occurrence of singlet–singlet Förster-type energy transfer within the reactants. In addition, no static quenching was observed. At 77 K, the isc process seems to be primarily responsible for the observed decrease in the donor fluorescence emission band in the presence of DMTP, whereas triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer appears to be responsible for donor phosphorescence quenching. © 1998 Elsevier Science S.A.

Keywords: Electron transfer; Energy transfer; Fluorescence quenching; Intersystem crossing; Phosphorescence quenching

1. Introduction

Studies on the radiationless transitions from the excited electronic states of various organic donors due to photoinduced electron transfer (PET) reactions with suitable acceptors and other concurrent processes are still the subject of great interest to photophysicists and photochemists [1–10]. The quenching reactions in bimolecular cases are generally found to proceed through two mechanisms: excitational energy transfer and PET processes. These two processes are the basic quenching reactions. Both energy transfer and electron transfer (ET), especially the latter, have a central position in chemistry and biochemistry. ET reactions are involved in photosynthesis, metabolism and in simple chemical reactions [11–15]. In most bimolecular reactions (between electron donor and acceptor molecules), concurrent occurrence of the two processes, energy transfer and ET, can be observed, especially when the donor chromophore is excited [1,16].

Photoinduced intermolecular or intramolecular ET reactions are normally performed in a highly polar solvent, e.g. acetonitrile (ACN), which facilitates the formation of solvent-separated radical ions or free ions [7–9,17,18]. When ET reactions occur between excited (or ground) state electron donor and ground (or excited) state electron acceptor molecules, the primary intermediate is a geminate ion pair (GIP) complex: contact/tight ion pair (CIP) or extended/loose ion pair (LIP). As reported by Mataga and Shioyama [19], direct excitation of the ground state electron donor–acceptor charge transfer (CT) complex leads to the formation of a CIP, whereas a LIP is formed due to singlet excitation of either donor or acceptor moiety. In most cases, these complexes (or exciplexes) are of non-emissive type and can only be detected by picosecond/femtosecond spectroscopic techniques [18]. Thus, due to secondary ET processes, we should expect the formation of free radical ions in the case of a LIP complex. This phenomenon is generally observed in ACN. In a CIP complex, geminate recombination (back ET) results in the formation of either ground or triplet donor/acceptor species. In bichromophoric systems of donor and acceptor,

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which are linked by a covalent spacer (UV transparent), this back ET reaction is known as the energy wasting process [20].

It has been reported previously [18] that, in several alkylcarbazole–polynitrofluorene and alkylcarbazole–polynitrofluorenone bichromophoric systems, the rates of charge separation are very high (approximately 10^{11}–10^{12} s^{-1}) relative to the charge recombination (back ET) rate constants (approximately 10^{8} s^{-1}), which shows good electron transport in these bichromophoric systems. Recently, our laboratory has been involved in systematic steady state and time-resolved studies of different organic donors and well-known acceptors to reveal the nature of the intermolecular ET mechanism within these systems at both ambient (296 K) and low (77 K) temperatures. These studies are currently being made in anticipation that the mechanisms of intramolecular ET reactions within these donor–acceptor systems will be better understood when they are connected, in future, by flexible polymethylene (σ-type) or carotenoid (π-type) spacers. Investigations on intramolecular systems are of interest in the development of highly efficient photoconducting materials which should have wide applications in the electrophotographic/xerographic industry. Moreover, using bichromophoric systems in which efficient ET reactions occur, molecular electronic devices may be built.

In previous work [7–9], tetracyanoquinodimethane (TCNQ) was mainly used as electron acceptor. In the present work, we have chosen another well-known acceptor, dimethylterephthalate (DMTP), which has been used previously by several workers to investigate PET reactions with various organic electron donors, in particular carbazoles [21,22]. In this investigation, *p*-toluidine (p-tol) and *N,N*-dimethyl-*p*-toluidine (N,N-DM-p-tol) were used as donors because the photophysical properties of these donor systems are well documented in the literature [23].

In this investigation, using the above electron donors and acceptor, bimolecular quenching reactions were studied in both polar ACN and non-polar *n*-heptane fluid solutions at ambient temperature and in ethanol (EtOH) rigid glassy matrix at 77 K employing electronic absorption and steady state and time-resolved luminescence techniques. The low temperature (77 K) measurements were performed to determine whether the conformational changes, occurring via the orientation of the $-NH_2$ group [23–25], of the donor molecules have any effect on their photophysical properties in the electronic excited singlet (S_1) and triplet (T_1) states. The different non-radiative processes, at both room and low temperature (77 K), resulting from the interactions between the donor and acceptor molecules, and also due to conformational changes of the donor molecules, were carefully examined and are reported.

2. Experimental details

2.1. Purification of chemicals

Samples of p-tol (obtained from British Drug House), N,N-DM-p-tol and DMTP (both supplied by Aldrich) were purified by vacuum sublimation. The solvents *n*-heptane, ACN and EtOH (E. Merck) of spectroscopic grade were distilled under vacuum.

2.2. Spectroscopic apparatus

The room temperature electronic absorption and steady state emission spectra of moderate to very dilute solutions (approximately 10^{-3}–10^{-5} M) of the samples were recorded using a Shimadzu UV-visible 2101PC spectrophotometer and a Perkin–Elmer MPF 44A fluorescence spectrophotometer respectively. The excitation wavelengths selected for emission of both electron donors, p-tol and N,N-DM-p-tol, at 296 and 77 K were 315 nm and 308 nm respectively (DMTP absorbance was found to be negligible at these temperatures). The fluorescence lifetimes of the samples were measured using a time-correlated, single-photon counting (TCSPC) fluorimeter constructed from components purchased from Edinburgh Analytical Instruments (EAI). The measurements were made in a conventional L-format arrangement. This instrument closely resembles Edinburgh Instruments model 199, UK. The excitation source consisted of an all-metal coaxial N_2 flash lamp with an instrumental response function of about 1.3 ns full width at half-maximum (FWHM) at a repetition rate of 25 kHz. The fluorescence decay curves were analysed using an impulse deconvolution fit. The goodness of fit was assessed over the entire decay, including the rising edge, and was tested with a plot of the weighted residuals, reduced χ^2 values and the Durbin–Watson (DW) parameters.

All solutions for the room temperature measurements were deoxygenated by irrigating with an N_2 gas stream for about 30 min. Electrochemical measurements were performed using the PAR 370-4 electrochemistry system, the details of which are given elsewhere [7].

3. Results and discussion

3.1. Electronic absorption spectra of the electron donors p-tol and N,N-DM-p-tol in the presence of the acceptor DMTP in different fluid solutions at ambient temperature

It is apparent from Fig. 1 that the absorption spectrum of the mixture of p-tol (or N,N-DM-p-tol) and DMTP in polar ACN (or non-polar *n*-heptane) fluid solution is the superposition of the individual bands of the donor and acceptor. This observation excludes the possibility of the formation of a ground state CT complex between the donor and acceptor molecules.

3.2. Measurements of the steady state fluorescence emission spectra of the donors and their fluorescence lifetimes by the TCSPC method at ambient temperature in the presence of the acceptor DMTP

DMTP is an efficient electron acceptor [21,26–31] and is capable of quenching the excited state of a suitable donor

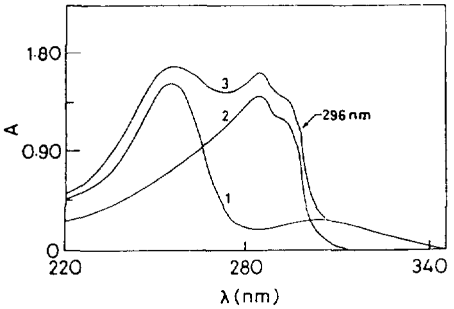


Fig. 1. Electronic absorption spectra of p-tol ($C=5.2\times10^{-5}$ M, $l=1$ cm) (curve 1), DMTP ($C=2.0\times10^{-4}$ M, $l=1$ cm) (curve 2) and p-tol ($C=5.2\times10^{-5}$ M, $l=1$ cm) in the presence of DMTP ($C=2.0\times10^{-4}$ M) (curve 3) in ACN fluid solution at 296 K.

through strong ET reaction. Thus the following studies were performed to observe the changes, if any, in the nature of the fluorescence spectra of the donors in the presence of the acceptor DMTP. Excitation of the donor was made selectively in the presence of the acceptor using an excitation wavelength of 315 nm (Fig. 1). It should be noted that the absorbance of DMTP at 315 nm is negligible. Under these conditions, the steady state fluorescence emission spectrum of p-tol in ACN fluid solution (curve 0, Fig. 2(a)) shows a peak at around 338 nm. It should be noted that DMTP gives no room temperature fluorescence. A gradual reduction of the fluorescence emission intensity of p-tol (or N,N-DM-p-tol) is observed on addition of DMTP (Figs. 2(a) and 2(b)). This fluorescence quenching is accompanied by a slight, but definite, blue shift of the spectra. As quenching occurs at higher concentrations of DMTP (approximately 10^{-3}–10^{-2} M, Figs. 2(a) and 2(b)), it is logical to presume that an inner-filter effect may take place at these concentrations. The steady state intensity corrections due to the inner-filter effect were made using the following expression [32]

$$f_{\mathrm{corr}}=f_{\mathrm{obs}}\ \mathrm{antilog}\left(\frac{\mathrm{OD}_{\mathrm{ex}}^{\mathrm{q}}}{2}\right)$$

where $\mathrm{OD}_{\mathrm{ex}}{}^{\mathrm{q}}$ is the absorbance of the quencher at the excitation wavelength.

As the concentration of the acceptor, used in the fluorescence measurements, does not affect the electronic absorption spectral pattern (both in terms of the intensity and energy position) of the donor molecule, the possibility that the formation of a ground state complex may be responsible for the observed donor fluorescence quenching can be ruled out. However, the following routes of non-radiative deactivation of the excited singlet (S_1) state of the donor in the presence of the acceptor DMTP should be examined: (1) PET from the excited donor to the ground state acceptor; (2) excitational energy transfer from the excited donor to the acceptor; (3) static quenching.

It is apparent from Fig. 3(a) that the fluorescence quenching of the donors in the presence of the acceptor DMTP obeys the simple Stern–Volmer (SV) relation

$$f_0/f=1+K_{\mathrm{SV}}[\mathrm{Q}] \tag{1}$$

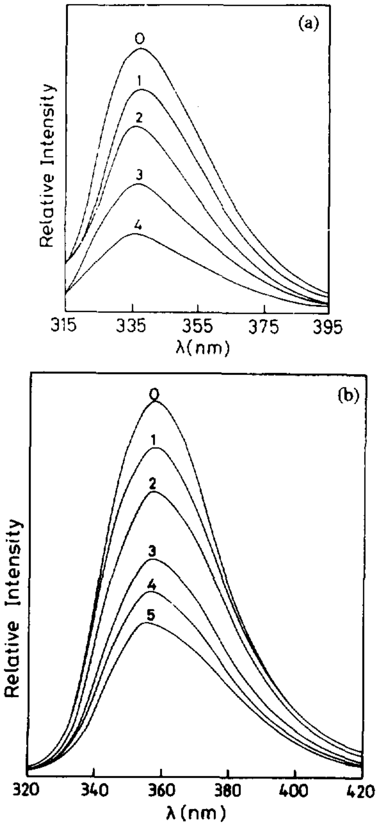


Fig. 2. (a) Fluorescence emission spectra of p-tol in ACN fluid solution ($C=4.4\times10^{-5}$ M) at 296 K ($\lambda_{\mathrm{exc}}=315$ nm) in the presence of DMTP. Concentration of DMTP (M): 0, 0; 1, 1.1×10^{-3}; 2, 2.8×10^{-3}; 3, 8.5×10^{-3}; 4, 1.7×10^{-2}. (b) Fluorescence emission spectra of N,N-DM-p-tol in ACN fluid solution ($C=5.2\times10^{-5}$ M) at 296 K ($\lambda_{\mathrm{exc}}=306$ nm) in the presence of DMTP. Concentration of DMTP (M): 0, 0; 1, 2.4×10^{-4}; 2, 9.7×10^{-4}; 3, 2.4×10^{-3}; 4, 3.6×10^{-3}; 5, 4.8×10^{-3}.

In Eq. (1), f_0 and f (inner-filter effect corrected) represent the relative integrated fluorescence emission intensities of the donor in the absence and presence of the quencher ([Q]) respectively. These f_0 and f values were measured from the corrected area under the fluorescence curves. K_{SV} ($=k_{\mathrm{q}}\tau_0$) is the SV constant, k_{q} denotes the observed dynamic fluorescence quenching rate constant and τ_0 is the fluorescence lifetime of the donor in the absence of the acceptor. The τ_0 values of the donors, measured by the TCSPC method, together with K_{SV} and k_{q}, are shown in Table 1.

From the good linear SV plots (intensity quenching plots, Fig. 3(a)), we may logically presume that the quenching is of dynamic type and that the static quenching effect is absent. However, to corroborate this proposition, another form of the SV relation (Eq. (2)) was used

$$\tau_0/\tau=1+K_{\mathrm{SV}}[\mathrm{Q}] \tag{2}$$

where τ_0 and τ are the fluorescence lifetimes of the donor (fluorescer) in the absence and presence of the quencher ([Q]) respectively. It is observed that $f_0/f\approx\tau_0/\tau$. For the donor–acceptor pairs used, the k_{q} values obtained from the plots of τ_0/τ vs. [Q] (Fig. 3(b)) are more or less similar (within experimental error) to the corresponding values

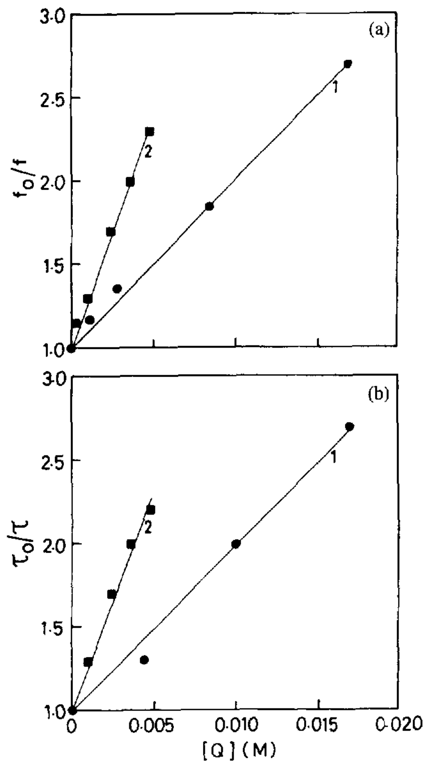


Fig. 3. Simple Stern–Volmer (SV) plots of p-tol in the presence of DMTP (curve 1) and N,N-DM-p-tol in the presence of DMTP (curve 2) in ACN fluid solution at 296 K using: (a) Eq. (1) and (b) Eq. (2) (see text).

obtained from the steady state (using Eq. (1)) quenching experiment as discussed above (Table 1). These observations indicate that the static quenching effect within the donor–acceptor systems is absent and that the quenching is of dynamic type.

As there is a lack of overlap between the emission spectrum of the donor (p-tol or N,N-DM-p-tol) and the electronic absorption spectrum of the acceptor DMTP, the possibility of occurrence of a singlet–singlet ($S_1^D \rightarrow S_1^A$) energy transfer process by Förster's dipole–dipole mechanism can be ruled out.

The possibility of a forward ET reaction between the excited donor and ground state acceptor molecules can be measured in terms of the Gibbs free energy change ΔG^0 accompanying the singlet excited state ET reaction. The free energy change ΔG^0 associated with radical ion pair formation can be determined from the well-known Rehm–Weller relation [18,33,34]

$$\Delta G^0 = E_{1/2}^{\mathrm{OX}}(\mathrm{D/D^+}) - E_{1/2}^{\mathrm{RED}}(\mathrm{A^-/A}) - E_{0,0}^{*} - e^2/(4\pi\epsilon_0\epsilon_s R) \tag{3}$$

where the symbols have their usual meanings.

In highly polar solvents, such as ACN, the coulombic term is negligible [1,18]; therefore the ΔG^0 values were computed by neglecting the fourth term in Eq. (3). Table 2 shows that, when the donor is in the electronic excited state, $\Delta G^0 < 0$, indicating that the ET reaction from the excited donor to the acceptor is highly exergonic and thus energetically favourable [35,36]. The positive values of ΔG^0 when both donor and acceptor are in the ground state (Table 2) indicate that the probability of occurrence of the ET reaction between the unexcited donor and acceptor molecules is small.

In polar solvents, fluorescence quenching by ET follows the reaction path depicted in Scheme 1 (PATH 1) [33,34,37]. In Scheme 1 (PATH 1), k_d and k_{-d} are the diffusion-controlled rate constants of second and first order respectively, k_{ET} and k_{-ET} are the first-order rate constants for charge separation in the "precursor complex" and charge recombination in the "successor complex" respectively and k_s is the first-order rate constant for the dissociation of the successor complex. Rehm and Weller [33,34] have determined that, for many organic reacting pairs, the magnitude of the fluorescence quenching rate constant by ET is diffusion limited ($k_q \sim 2.0 \times 10^{10}$ M^{-1} s^{-1}) for $\Delta G^0 < -10$ kcal mol^{-1} (-0.434 eV) and remains constant as ΔG^0 becomes more and more negative (more exothermic). For the present donor–acceptor systems (p-tol/N,N-DM-p-tol–DMTP), k_q for the ET reaction can be calculated from the empirically derived expression [1,33,34]

Table 1

Comparison of the fluorescence quenching rate constant (k_q) with the driving force (ΔG^0) for different donor (in the excited electronic state S_1) and acceptor (in the ground electronic state S_0) pairs in ACN fluid solution at 296 K (τ_0 is the fluorescence decay time of the donor molecule at 296 K in the absence of the quencher)

System	τ_0 (±0.4) (ns)	Fluorescence intensity measurements		Fluorescence lifetime measurements		Empirical relations (4) and (5)^a	
		K_{SV} (M^{-1})	k_q (M^{-1} s^{-1})	K_{SV} (M^{-1})	k_q (M^{-1} s^{-1})	k_q(ET) (M^{-1} s^{-1})	ΔG^0 (eV)
p-tol* + ACN	3.2						
p-tol* + DMTP + ACN		101	3.2×10^{10}	106	3.3×10^{10}	1.6×10^{10}	−2.41
N,N-DM-p-tol* + ACN	3.1						
N,N-DM-p-tol* + DMTP + ACN		277	8.9×10^{10}	268	8.6×10^{10}	1.5×10^{10}	−2.51

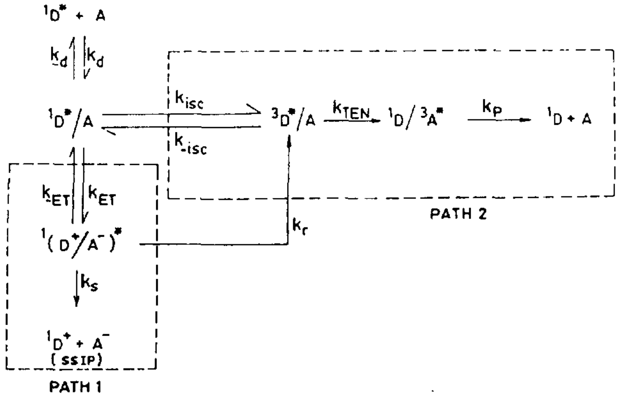
Asterisk denotes the first electronic excited state (S_1).

^{a}See text.

Table 2
Redox potentials and Gibbs free energies (ΔG^0) for different donor–acceptor pairs in ACN fluid solution at 296 K

Donor	Acceptor	$E_{1/2}^{OX}(D/D^+)$ (V)	$E_{1/2}^{RED}(A^-/A)$ (V)	$E_{0,0}^*$ (eV)	ΔG^0 (eV)	Average of ΔG^0 (eV)
p-tol*	DMTP	0.81	−0.93	4.20 (295 nm)	−2.47	−2.41
				4.06 (305 nm)	−2.34	
p-tol	DMTP	0.81	−0.93		+1.73	
N,N-DM-p-tol*	DMTP	0.70	−0.93	4.20 (295 nm)	−2.58	−2.51
				4.05 (306 nm)	−2.43	
N,N-DM-p-tol	DMTP	0.70	−0.93		+1.63	

Asterisk denotes the first electronic excited state (S_1).



SSIP: Solvent-separated radical ion pair

Scheme 1.

$$k_q(\mathrm{ET}) = \frac{2.0\times10^{10}}{1+0.25[\exp(\Delta G^{\dagger}/kT)+\exp(\Delta G^0/kT)]}\ (\mathrm{M^{-1}\,s^{-1}}) \tag{4}$$

where $\Delta G^{\dagger}$ is the activation free enthalpy of the ET reaction when one of the molecules is in the excited singlet state. It is calculated by the following empirical relation [1,33,34]

$$\Delta G^{\dagger} = \frac{\Delta G^0}{2} + \left[\left(\frac{\Delta G^0}{2}\right)^2 + \{\Delta G^{\dagger}(0)\}^2\right]^{1/2} \tag{5}$$

in which $\Delta G^{\dagger}(0) = 0.104$ eV at $\Delta G^0 = 0$.

The values of k_q calculated using Eqs. (4) and (5) are presented in Table 1. The observed values of k_q (from both fluorescence intensity and lifetime measurements) for the donor–acceptor pairs are somewhat larger (especially in the case of N,N-DM-p-tol) than the corresponding values of k_q computed using the empirical relations (4) and (5). This discrepancy indicates that a process in addition to ET must be involved in the fluorescence quenching mechanism of the donors in the presence of the acceptor DMTP. One possible explanation is given below.

On going back to Figs. 2(a) and 2(b), we can observe a regular decrease in the fluorescence emission intensity of the donor molecule (p-tol and N,N-DM-p-tol), accompanied by a gradual blue shift of the spectrum, in ACN fluid solution with increasing concentration of DMTP. The effects of conformational changes in aniline and related compounds on the spin-forbidden electronic transitions have been studied previously [23,38]. From these studies on the photophysical properties of aniline/substituted aniline compounds in solvents of different polarity at different temperatures (starting from ambient temperature down to the solvent stiffening range 140–77 K) [23,38], it was observed that the orientation of the $-NH_2$ group in aromatic amines had a great influence on the spin-forbidden electronic transitions, such as intersystem crossing (isc). In the case of phenetidine compounds, Jana and Ganguly [24] have reported that, due to the orientation of the $-NH_2$ group, the lowest excited singlet state (S_1), which is initially of $\pi\pi^*$ nature, acquires $n\pi^*$ character; as the triplet of these molecules still retains its $\pi\pi^*$ property, the isc rate is enhanced considerably between S_1 ($n\pi^*$) and T_1 ($\pi\pi^*$) due to their different nature [25]. However, in addition to temperature, an increase in solvent polarity may lead to conformational changes in aniline compounds by making the $-NH_2$ group more coplanar with the aromatic ring [24] and, as a result, both the S_2 and S_1 states may acquire some $n\pi^*$ character. In the present investigation, it is possible that, due to the gradual addition of DMTP to ACN, the polarity of the mixture may be increased. This may change the orientation of the $-NH_2$ group (or $-N(CH_3)_2$ in the case of N,N-DM-p-tol) of the donor molecules in such a way that the lowest excited singlet (S_1) may acquire $n\pi^*$ character, resulting in the enhancement of the isc rate from this state to the triplet (T_1), the latter being of $\pi\pi^*$ nature (confirmed by phosphorescence lifetime (τ_p) measurements of the donor molecules; the τ_p values were found to be of the order of seconds, which is indicative of the $\pi\pi^*$ nature of the donor triplet (T_1)). Supporting evidence in favour of the $n\pi^*$ character of the singlet states is that, with increasing polarity of the medium (due to the addition of DMTP to ACN), a blue shift in the room temperature fluorescence emission spectrum is observed (Figs. 2(a) and 2(b)).

Thus, from the above observations, it may be inferred that, at ambient temperature, the probable routes through which the excited singlet states of the donor molecules deactivate non-radiatively in the presence of the acceptor DMTP in ACN fluid solution are: (1) PET (PATH 1, Scheme 1) and (2) isc (PATH 2, Scheme 1). Possibly due to the combined effect of these two processes, larger fluorescence quenching rates (Table 1) than those expected if only the ET process was involved were observed. In Scheme 1, k_r is the rate of the charge recombination process producing triplet state donor molecules, k_{isc} is the first-order isc rate of the donor and k_{TEN} is the rate constant associated with triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer from the donor to the acceptor. This type of energy transfer was confirmed in this study by low temperature (77 K) measurements in an EtOH rigid glassy matrix. The details of these studies are given in the next section. k_p is the first-order phosphorescence decay rate constant. The other symbols have already been discussed.

In this investigation, from the observed blue shift of the donor fluorescence in the presence of the acceptor DMTP at both ambient temperature and 77 K (see below), it seems that the isc process (PATH 2, Scheme 1) is mainly responsible for the production of donor triplets. Moreover, in polar ACN solvent, k_s is generally much greater than k_r (Scheme 1). Hence, in this solvent, the probability of the formation of triplet donors from charge recombination is very small.

As discussed above, the observed value of k_q for N,N-DM-p-tol–DMTP is somewhat higher (8.9×10^{10} M^{-1} s^{-1}, Table 1) than that for p-tol–DMTP (3.2×10^{10} M^{-1} s^{-1}, Table 1). At the present stage of investigation, it is rather difficult to propose conclusively any mechanism for this large quenching effect of the dimethyl-substituted p-tol donor. However, the larger percentage in the CT configuration in both excited electronic states S_1 and S_2 [39] of the *N*,*N*-dialkyl-substituted derivative, in comparison with its parent analogue aniline, may be responsible for the larger observed k_q value (Table 1) in the case of the N,N-DM-p-tol donor molecule; due to the larger CT character of the excited singlet states, an additional isc process may contribute to the fluorescence quenching mechanism of this molecule. Thus, at room temperature, the overall quenching rate (k_q) for the donor–acceptor pairs can be expressed as

$$k_q = k_q(\mathrm{ET}) + k_q(\mathrm{isc}) \qquad (6)$$

The contribution of the second term on the right-hand side of Eq. (6) appears to be relatively larger for N,N-DM-p-tol in comparison with p-tol.

As at low temperature (140–77 K, the solvent stiffening range) aniline compounds suffer large conformational changes through orientation of the $-NH_2$ group [26,31], it seemed worthwhile to study the low temperature interactions between the donor and acceptor molecules. The results are described below.

3.3. Nature of the electronic states and spectral features at 77 K of the donors p-tol and N,N-DM-p-tol in the presence of the acceptor DMTP: measurements made by steady state and time-resolved methods

Singlet excitation of p-tol in an EtOH rigid glassy matrix at 77 K gives rise to fluorescence and broad phosphorescence emission spectra with maxima at 335 nm and 410 nm respectively (Figs. 4(a) and 4(b)). The low temperature (77 K) emission spectrum of DMTP in an EtOH rigid glassy matrix exhibits weak phosphorescence (Fig. 4(c)). Selective excitation of p-tol (or N,N-DM-p-tol) in the presence of DMTP results in a reduction in the fluorescence emission intensity of the former molecule, accompanied by a blue shift (Fig. 4(a)). A further reduction in intensity is observed when the concentration of DMTP is increased. It seems that this blue shift is caused by the increase in polarity (due to the addition of DMTP ($\epsilon \sim 8.5$) to EtOH ($\epsilon \sim 24.55$)) of the environment, which indicates that the lowest excited singlet state (S_1) of p-tol (or N,N-DM-p-tol) may acquire, possibly due to conformational changes, $n\pi^*$ character at 77 K in the presence of DMTP. Thus, the observed lowering of the fluorescence emission intensity of the donor at 77 K may logically be assumed to be due to the efficient isc process from the S_1 state, as the donor triplet (T_1) retains its $\pi\pi^*$ character (lifetimes of the order of seconds, Table 3) [25]. On the other hand, because ET is a thermally activated process, it is

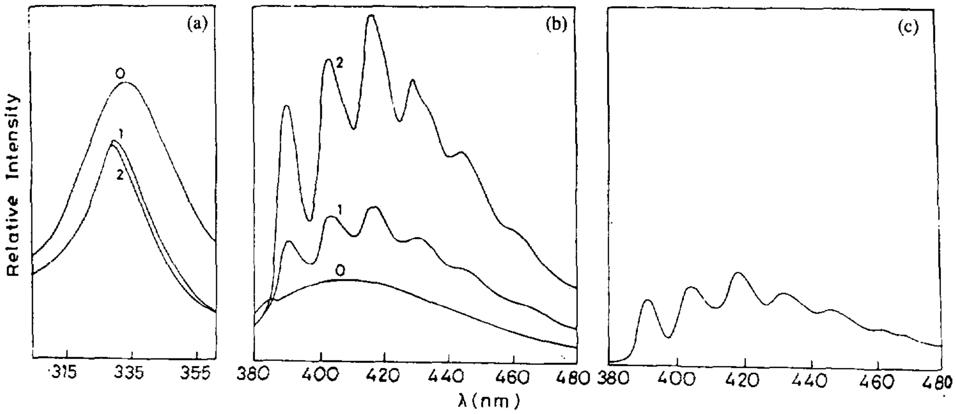


Fig. 4. (a) Fluorescence emission spectra of p-tol in EtOH rigid glassy matrix ($C = 4.6 \times 10^{-5}$ M) at 77 K ($\lambda_{exc} = 308$ nm) in the presence of DMTP. Concentration of DMTP (M): 0, 0; 1, 3.1×10^{-4}; 2, 1.0×10^{-3}. (b) Phosphorescence emission spectra of p-tol in EtOH rigid glassy matrix ($C = 7.4 \times 10^{-5}$ M) at 77 K ($\lambda_{exc} = 308$ nm) in the presence of DMTP. Concentration of DMTP (M): 0, 0; 1, 1.0×10^{-4}; 2, 5.1×10^{-4}. (c) Phosphorescence emission spectrum of DMTP in EtOH rigid glassy matrix ($C = 1.0 \times 10^{-4}$ M) at 77 K ($\lambda_{exc} = 308$ nm).

Table 3
Phosphorescence lifetimes (τ_p) of the donor–acceptor systems in EtOH rigid glassy matrix at 77 K

System	τ_p (±10%) (s) at λ_{em}	
	418 nm	448 nm
p-tol* + EtOH	5.7	5.5
DMTP* + EtOH	2.8	3.2
p-tol* + DMTP + EtOH	3.4	3.2
N,N-DM-p-tol* + DMTP + EtOH	3.4	3.3

Asterisk denotes the first excited triplet state (T_1).

expected to play a minor role in the fluorescence quenching of the donor in the presence of the acceptor DMTP at 77 K [40]. Interestingly, the phosphorescence spectrum (produced by excitation of the donor moiety) of a mixture of p-tol and DMTP in an EtOH rigid glassy matrix at 77 K exhibits only structured phosphorescence similar to that of DMTP (Fig. 4(b)). As the phosphorescence lifetimes τ_p, measured at different wavelengths of this phosphorescence band, are very similar to the lifetime of the acceptor DMTP (Table 3), it is safe to assign this band to the phosphorescence of the acceptor DMTP. Thus, from the above observations, it appears that a triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer process may be responsible for the observed quenching of the donor phosphorescence emission band, with the concomitant appearance of the phosphorescence of the acceptor DMTP.

4. Conclusions

At ambient temperature, no evidence for the formation of a ground state CT complex between the donor and acceptor was found.

The strong quenching of the excited singlet state (S_1) of the donor in the presence of the acceptor DMTP at 296 K was found to be due to: (1) PET reactions between the excited donor and ground state acceptor and (2) an increase in the isc process within the donor in the presence of the acceptor DMTP due to conformational changes of the former molecule. No significant singlet–singlet energy transfer process was operative here due to a lack of spectral overlap between the donor emission and acceptor DMTP absorption. In addition, no evidence for static quenching was found. It is speculated that, in the case of N,N-DM-p-tol, another process, in addition to (1) and (2), may be responsible for fluorescence quenching; this may be a result of the larger CT configurational changes, relative to p-tol, of the lowest electronic excited singlet state S_1.

It is proposed that process (2) may be primarily responsible for low temperature (77 K) donor fluorescence quenching phenomena in the presence of the acceptor DMTP, whereas $T_1^D \rightarrow T_1^A$ energy transfer appears to be responsible for the phosphorescence quenching of the donor molecule together with the concomitant appearance and enhancement of the phosphorescence band of the acceptor on addition of the latter to a mixture of donor and EtOH.

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