

EXCITED STATE INTERACTION BETWEEN 2-*N,N*-DIMETHYLAMINO-PYRIDINE AND *p*-NITROANILINE

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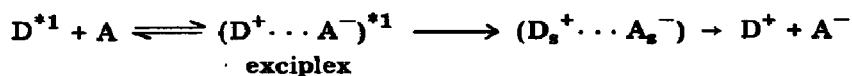
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Summary

Fluorescence quenching of 2-*N,N*-dimethylaminopyridine induced by *p*-nitroaniline is shown to arise from exciplex formation. The fluorescence wavelength maximum of the exciplex in ether-isopentane-ethanol solutions is 425 nm for 2-*N,N*-dimethylaminopyridine and 410 nm for 2-amino-pyridine, reflecting a smaller ionization potential in the former. Flash photolysis studies suggest that exciplex formation results in enhanced triplet population of the *p*-nitroaniline, which has the lowest triplet in this system.

1. Introduction

Research in exciplex phenomena has remained a subject of continuing interest [1]. The proof of excited state interaction usually involves demonstrating the presence of a new emitting species or a photochemical event evolving from the interacting pair of donor and acceptor molecules. Triplet exciplexes are not as commonly observed as their singlet counterparts, especially in low temperature glasses where diffusion is absent. The processes available to exciplex singlets formed from an excited donor D^* and a ground state acceptor molecule A are summarized in Scheme 1 where the various decay modes are given.



*Decay modes from D^{*1}*

- (1) $D + A + h\nu_f(D)$
- (2) $D + A$
- (3a) $D^{*3} + A$
- (3b) $D + A^{*3}$
- (4) $D + A^{*1}$

Decay modes from exciplex

- (1') $D + A + h\nu_f'(DA)$
- (2') $D + A$
- (3'a) $D^{*3} + A$
- (3'b) $D + A^{*3}$

Scheme 1.

The exciplex fluorescence appears at longer wavelengths than the fluorescence of the excited electron donor or acceptor and the formation of ions is favored in polar solvents such as acetonitrile. Decay channels (1) and (1') represent the most direct way of studying such systems. The generation of ions was demonstrated many years ago by Leonhardt and Weller [2] using flash photolysis techniques. In a previous study [3] we have reported that the fluorescence of 2-aminopyridine can be quenched by *p*-nitroaniline in a process which involves exciplex formation and fluorescence. Excitation into the first excited singlet state of 2-aminopyridine was necessary to generate the exciplex. The singlet state of *p*-nitroaniline lies lower in energy and undergoes rapid radiationless decay. An energy level diagram of the system 2-aminopyridine (2-AMP) and *p*-nitroaniline (PNA) is given in Fig. 1 in which it can be seen that the singlet exciplex lies lower in energy than the singlet state of either the donor or the acceptor. Excitation at 366 nm did not give exciplex fluorescence. With the aim of understanding this type of excited state interaction we undertook a study of the system 2-*N,N*-dimethyl-AMP and PNA in ether-isopentane-ethanol (EPA) using fluorescence and flash photolysis techniques. The lower ionization potential of the *N*-dimethyl derivative compared with that of 2-AMP affords an additional parameter for understanding this behavior, since the exciplex fluorescence should appear at a lower energy in the former.

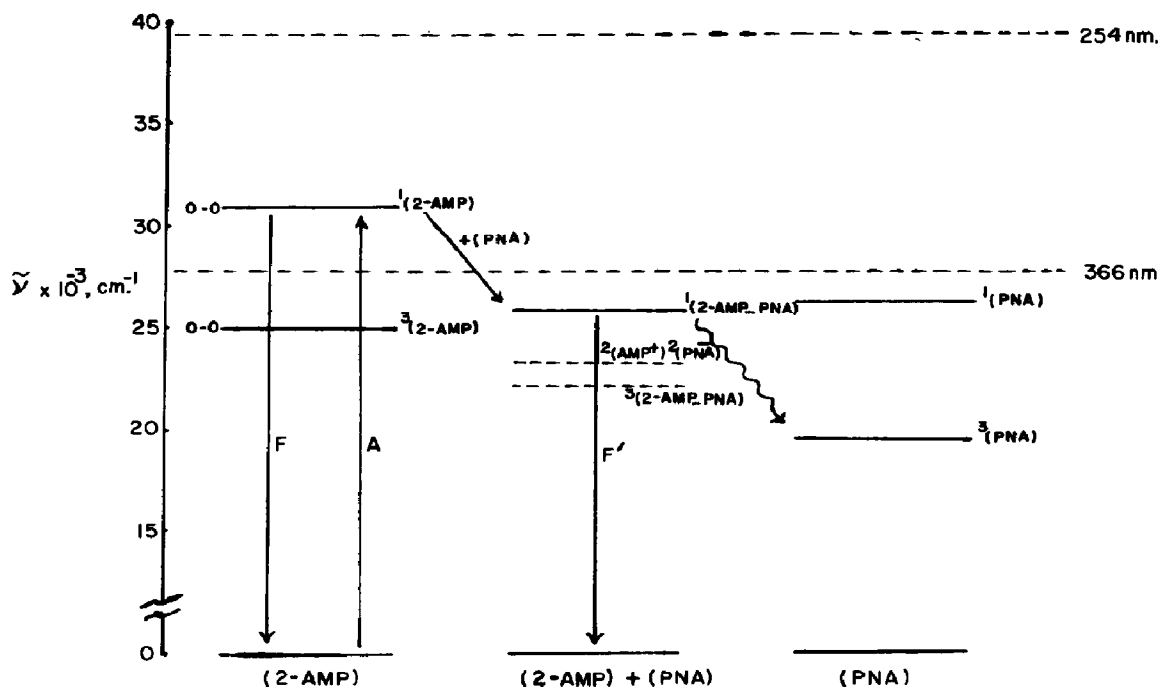


Fig. 1. An energy level diagram of the exciplex system 2-AMP and PNA. The energy levels indicated by solid lines were deduced from absorption and emission spectra.

2. Experimental

2.1. Materials

2-*N,N*-dimethyl-AMP was purified by vacuum distillation and PNA was purified by sublimation. Spectrograde EPA (ether, isopentane and ethanol in the volume ratio 5:5:2), obtained from Matheson, Coleman and Bell, was used as received after verifying that it contributed no impurity luminescence.

2.2. Instrumentation

Fluorescence measurements using 254 nm excitation were made with equipment which has been described elsewhere [4]. Flash photolysis experiments were performed on an apparatus previously described [5]. Solutions were vacuum degassed at 10^{-4} Torr prior to flashing. To avoid photochemical decomposition in the low temperature flash experiments, the solutions were cooled to -110 °C prior to flashing and, at this temperature, no absorbing transients were observed in the range 400 - 650 nm.

3. Results

The fluorescence of 4×10^{-4} M 2-*N,N*-dimethyl-AMP in EPA resulting from 254 nm excitation is shown in Fig. 2. Upon addition of PNA a decrease of the fluorescence intensity is initially observed. Continued addition of PNA results eventually in a new fluorescence with an emission wavelength maximum at approximately 425 nm. It can be seen that the fluorescence

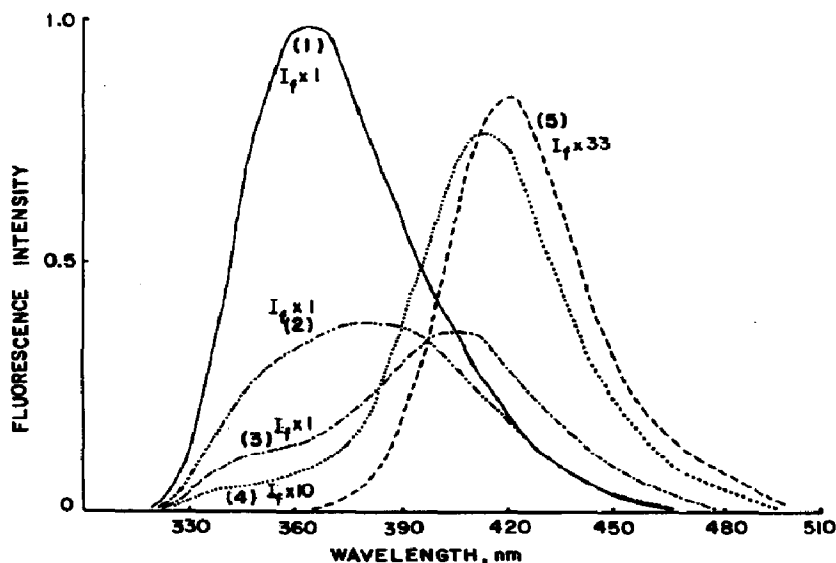


Fig. 2. Fluorescence spectra for degassed 4×10^{-4} M 2-*N,N*-dimethyl-AMP in EPA with increasing concentration of PNA and for 254 nm excitation: (1), no PNA; (2), 1.4×10^{-4} M PNA; (3), 2.1×10^{-4} M PNA; (4), 2.9×10^{-4} M PNA; (5), 7.24×10^{-4} M PNA.

yield of the exciplex is significantly smaller than that of 2-*N,N*-dimethyl-AMP ($\phi_f \approx 0.3 - 0.4$) [6]. This behavior is observed in both degassed and air-saturated solutions; however, the emission intensity of the long wavelength emission band is about 20% lower in the presence of air. The variation of the fluorescence intensity of 2-*N,N*-dimethyl-AMP with PNA concentration is given in Fig. 3. For this plot the concentration of the aminopyridines was held constant at 4×10^{-4} M and the concentration of PNA was varied. For the purpose of comparison a similar plot obtained for the fluorescence quenching of 2-AMP is included. It should be noted that the concentration value for 50% quenching is smaller for 2-*N,N*-dimethyl-AMP than it is for 2-AMP, *i.e.* 0.5×10^{-4} M and 1.5×10^{-4} M respectively.

The room temperature flash photolysis of degassed 2×10^{-4} M PNA in EPA results in a transient absorbing in the region 440 - 500 nm; this has been attributed [7] to the radical



When a degassed solution of 4×10^{-4} M 2-*N,N*-dimethyl-AMP in the presence of 2×10^{-4} M PNA is flashed, however, an overall intensification of the absorption occurs; this implies an increased concentration of PNA triplets, since the radical is believed to arise via the triplet state. The transient spectra observed with PNA alone and in the presence of 2-*N,N*-dimethyl-AMP are given in Fig. 4. The enhanced radical production that the exciplex affords should be noted. It was observed that the rate constant for decay was greater for the mixed solution than for PNA alone, *i.e.* 575 and 265 s^{-1} respectively. Attempts to observe ions in degassed acetonitrile, which is expected to favor ionization of the exciplex, were unsuccessful. No transient was observed in the region 400 - 600 nm when 2-*N,N*-dimethyl-AMP was flashed alone in EPA at room temperature.

Although UV absorption measurements of mixtures of these two molecules negate the presence of ground state complexes, we performed variable temperature flash studies to search for the presence of ions that might arise via electron transfer. Furthermore, the increased viscosity of EPA at low temperatures is expected to decrease diffusion, thereby preventing exciplex formation. Room temperature flash studies of the pair of molecules in EPA gave no evidence for ion production via charge transfer. In the range between -110 °C and -150 °C no transient was observed in the wavelength range 400 - 650 nm. The low temperature flash absorption data obtained in EPA for three different solutions are summarized in Fig. 5. Spectra (2) and (3) show the triplet-triplet absorptions for 4×10^{-4} M 2-*N,N*-dimethyl-AMP at -173 °C and 2×10^{-4} M PNA at -170 °C respectively. Spectrum (1) is obtained when a degassed solution containing the two molecules at these concentrations is flashed, indicating that the triplet-triplet absorption of each of the molecules is observed independently of the other, *i.e.* in the absence of diffusion the donor and acceptor do not generate exciplexes. The

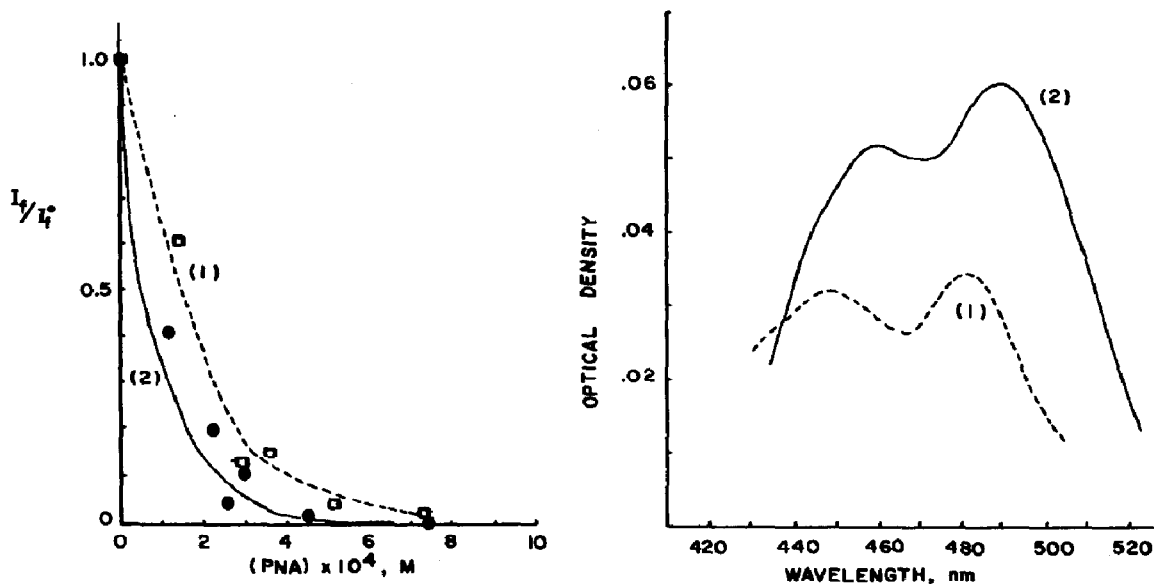


Fig. 3. The variation of the fluorescence intensity for EPA solutions of (1) 2-AMP (4×10^{-4} M) and (2) 2-*N,N*-dimethyl-AMP (4×10^{-4} M) in the presence of PNA with 254 nm excitation.

Fig. 4. Room temperature flash photolysis transient spectra for degassed EPA solutions of (1) 2×10^{-4} M PNA and (2) 2×10^{-4} M PNA with 4×10^{-4} M 2-*N,N*-dimethyl-AMP (12 cm absorption path length and 125 J flash^{-1}). The decay constants for the radical are $265 \pm 45 \text{ s}^{-1}$ and $575 \pm 68 \text{ s}^{-1}$ for solutions (1) and (2) respectively.

transient lifetime at -180°C of the long wavelength peak (590 nm) in spectrum (1) is approximately 4.5 ms, whilst the lifetime of the shorter wavelength peak (460 nm) is about 0.4 s, confirming that they arise from two different absorbing species. Lifetime data results indicate that there is no significant interaction between the triplet of PNA and 2-*N,N*-dimethyl-AMP in EPA at temperatures below -160°C .

4. Discussion

It is evident from the results that the fluorescence quenching of 2-*N,N*-dimethyl-AMP by PNA is caused by exciplex formation. In particular, the lower half-concentration value and the longer exciplex fluorescence wavelength maximum of 2-*N,N*-dimethyl-AMP relative to those of 2-AMP emphasize the charge transfer nature of the fluorescence quenching. The small half-concentration values for PNA quenching of 2-AMP and 2-*N,N*-dimethyl-AMP, which are 1.5×10^{-4} M and 0.5×10^{-4} M respectively, suggest that the equilibrium constant for exciplex formation is approximately 10^4 . This estimate is based on the assumption that the excited donor and exciplex have comparable lifetimes.

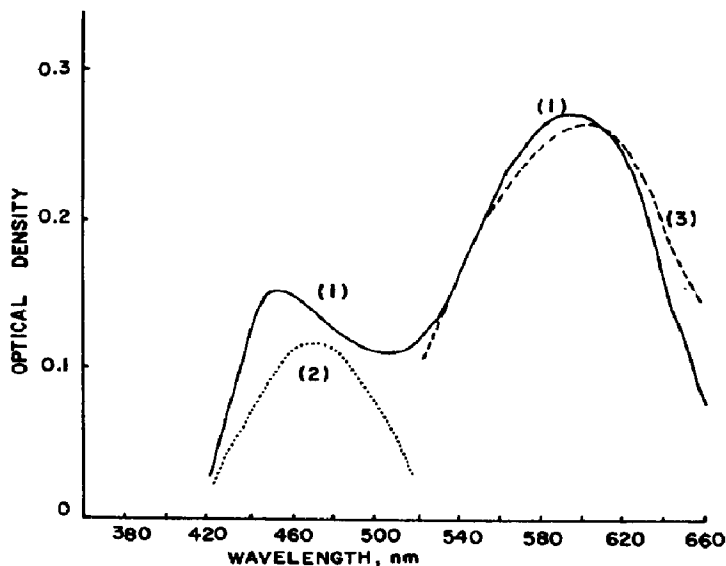
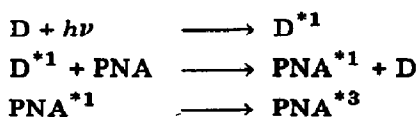


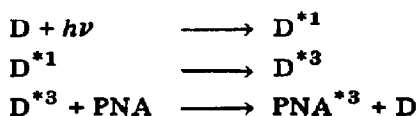
Fig. 5. Low temperature flash photolysis transient spectra in degassed EPA: (1), 2×10^{-4} M PNA and 4×10^{-4} M 2-*N,N*-dimethyl-AMP at -170°C , 125 J flash^{-1} ; (2), 4×10^{-4} M 2-*N,N*-dimethyl-AMP in EPA at -173°C , 80 J flash^{-1} ; (3), 2×10^{-4} M PNA in EPA at -170°C , 80 J flash^{-1} .

Energy transfer from the donor 2-*N,N*-dimethyl-AMP to generate triplets of PNA may proceed via the three following mechanisms:

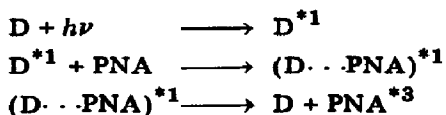
Mechanism 1



Mechanism 2



Mechanism 3



We consider that the second mechanism is unlikely since more than 90% of the fluorescence of 4×10^{-4} M 2-*N,N*-dimethyl-AMP is quenched at the concentration of PNA (2×10^{-4} M) used in the flash experiments. Neither mechanism 1 nor mechanism 3 can be eliminated as a possibility; however, the large estimated constant for exciplex formation (approximately 10^4 M^{-1}) suggests that mechanism 3 is the predominant mechanism of enhancing the triplet population of PNA. Singlet-singlet energy transfer to PNA, although

energetically possible, is difficult to verify since it is a non-fluorescent molecule. However, singlet-singlet energy transfer from 2-AMP to biacetyl has been demonstrated [8].

In view of the enhanced radical production of PNA upon addition of 2-*N,N*-dimethyl-AMP we suggest that the triplet of PNA is formed from the relaxed exciplex fluorescence state, as has been reported by Nishimura *et al.* [9] for the anthracene-*N,N*-diethylamine exciplex. The energy level diagram in Fig. 1 is also consistent with this view since the energy of the triplet state of PNA is lowest.

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