

## EXCIPLEX EMISSION FOR HYDROCARBON-DIMETHYLANILINE SYSTEMS IN HYDROXYLIC SOLVENTS

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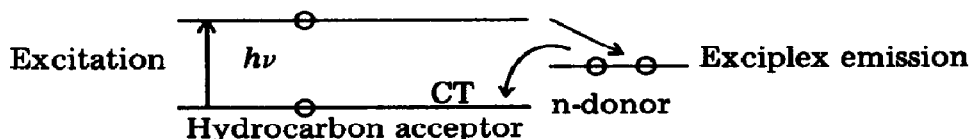
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### Summary

Exciplex emission from pyrene-dimethylaniline (DMA) and anthracene-DMA systems appears at a much lower wavelength in n-propanol ( $\epsilon = 20.1$ ) than in acetone ( $\epsilon = 20.7$ ). For all primary alcohols the exciplex emission appears at about the same position irrespective of the dielectric constants of the alcohols. However, the alcohols strongly quenched the exciplex emission in n-heptane and this quenching followed the Stern-Volmer relation. The quenching constants were found to follow the order primary > secondary > tertiary. These findings have been attributed to the stabilization of the non-bonding electrons at the nitrogen atom in DMA through hydrogen bonding with the alcohols.

The exciplex emissions from aromatic hydrocarbon-dimethylaniline (DMA) systems have been associated with the excited state charge transfer interaction in which DMA acts as a donor [1, 2]. As exciplex emission has also been reported from aromatic hydrocarbon-aliphatic triamine systems [3] it has been suggested that it is the non-bonding electron of the nitrogen in the amine which is transferred to the excited hydrocarbon molecule. We may propose the following energy level scheme for the charge transfer interaction and exciplex emission:



This level scheme is justified by the following approximate calculation. The energy of the highest field molecular orbital (MO) of anthracene is 7.56 eV and that of non-bonding electrons at nitrogen in aniline is 8.23 eV (data for DMA was not available). These are photoionization values [4]. Since the energy of the longest wavelength S-S transition in anthracene is 3.29 eV, the energy of the first empty MO of anthracene is placed at 10.85 eV. The exci-

plex emission energy in the above scheme is given as  $(10.85 - 8.23 =) 2.62$  eV (473 nm) which compares favourably with the exciplex emission from anthracene-DMA in n-heptane (which is located at 478 nm).

In the proposed scheme the frequency of the exciplex emission is determined by the position of the energy level of the non-bonding electron. If the energy of the non-bonding electron could be altered by some means, the exciplex emission frequency would change. It is a well-established fact that the non-bonding electrons of a hetero atom in an organic molecule are considerably stabilized in hydroxylic solvents through hydrogen bonding [5]. It is therefore expected that in alcoholic solvents the n-donor energy level will be lowered and the exciplex emission frequency will be increased, *i.e.* the exciplex emission will show a blue shift in hydroxylic solvents compared with the emission in non-hydroxylic solvents. Unfortunately all alcohols are highly polar and consequently the red shift associated with the reaction field stabilization of the exciplex [6, 7] as a whole will be superimposed on the blue shift associated with hydrogen bonding. If we could select two solvents

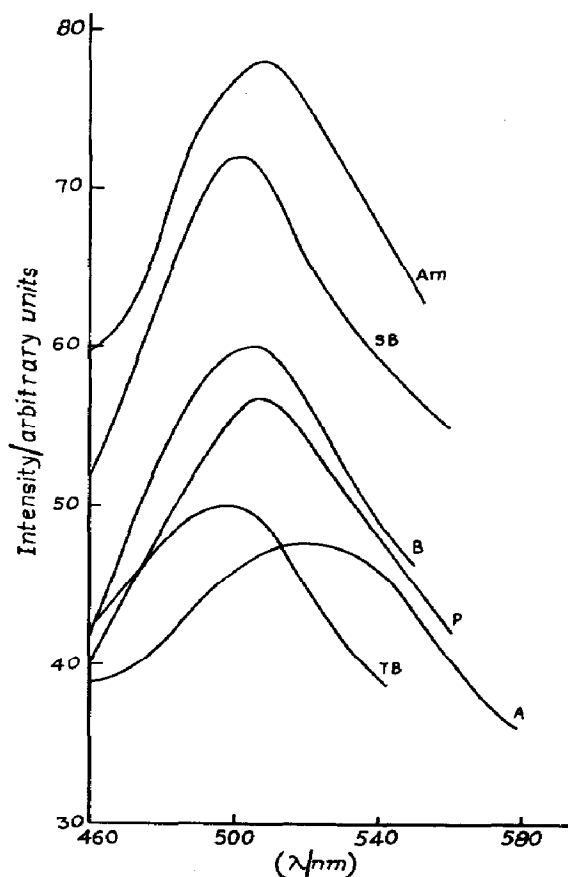


Fig. 1. Excimer emission from the  $2 \times 10^{-4}$  M pyrene-0.6 M DMA system in acetone (A), n-propyl alcohol (P), n-butyl alcohol (B), n-amyl alcohol (Am), sec-butyl alcohol (SB) and tert-butyl alcohol (TB).

with the same dielectric constant but of which only one could enter into hydrogen bond formation then the blue shift phenomenon would be detected in the exciplex emission. Now the dielectric constant of acetone is 20.7 and that of propyl alcohol is 20.1. Hence the reaction field stabilization will be about the same in both cases and the exciplex emission will appear at about the same position in the two solvents. The pyrene–DMA exciplex emission appeared at 522 nm in acetone but it appeared at 508 nm in *n*-propyl alcohol. For the anthracene–DMA system the exciplex emission appeared at 535 nm in acetone but at 520 nm in *n*-propyl alcohol. It appears therefore that the blue shift effect due to hydrogen bonding is present in these systems. Figures 1 and 2 give the exciplex emission spectra of the pyrene–DMA and anthracene–DMA systems in various hydroxylic solvents having a wide range of dielectric constants and the relevant data are summarized in Table 1. It may be observed that, irrespective of the dielectric constant, the exciplex emission appears at about the same position in all primary alcohols. This may be due

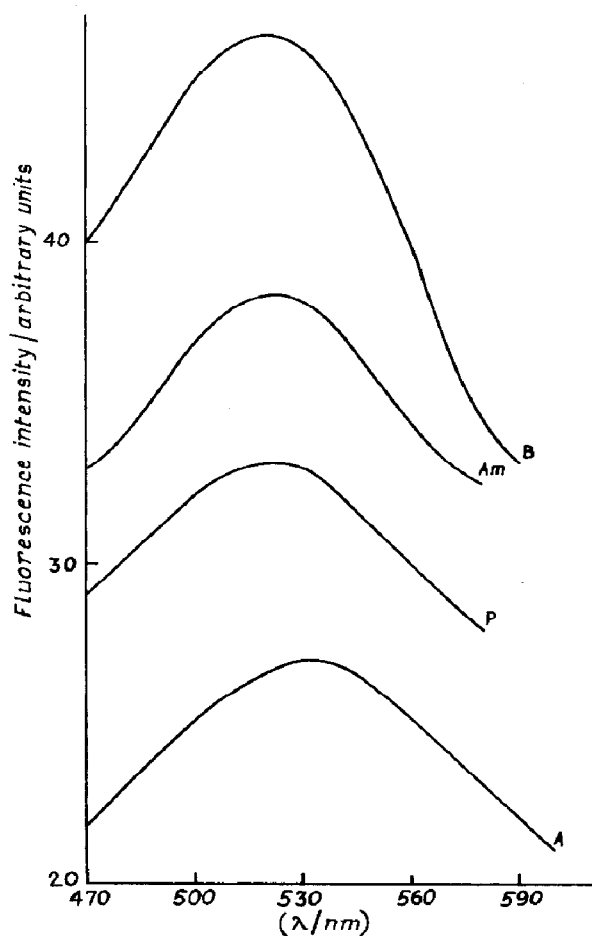


Fig. 2. Excimer emission from the  $2 \times 10^{-4}$  M anthracene–0.6 M DMA system in acetone (A), *n*-propyl alcohol (P), *n*-butyl alcohol (B) and *n*-amyl alcohol (Am).

TABLE 1  
Exciplex emission from hydrocarbon-DMA systems

Solvent	$\lambda_{\max}$ (nm)		$\epsilon$	$n$	$\eta$ (cP)
	Pyrene-DMA	Anthracene-DMA			
Acetone	522	535	20.7	1.358	0.316
n-Propyl alcohol	508	520	20.1	1.385	2.256
n-Butyl alcohol	505	520	17.8	1.399	2.948
n-Amyl alcohol	508	522	13.9	1.409	4.650
sec-Butyl alcohol	500	515	15.8	1.397	4.210
tert-Butyl alcohol	495	510	10.9	1.387	5.888

$\epsilon$ ,  $n$  and  $\eta$  were taken from International Critical Tables and refer to 25 °C.

to a balance between hydrogen bonding and the reaction field effect. That the reaction field stabilization in alcohol is considerable is shown by the fact that the exciplex emission in alcohol is considerably red shifted compared with the emission in n-heptane.

The exciplex emission in n-heptane was considerably quenched on addition of alcohol and the quenching followed the Stern-Volmer mechanism. Figure 3 gives a plot of  $f_0/f$  against  $[A]$  (where  $[A]$  is the alcohol concentration) for the pyrene-DMA system in n-heptane containing different amounts of n-butyl and tert-butyl alcohols. The quenching constants estimated from the slopes of the curves are summarized in Table 2. It may be observed that the quenching constants follow the order primary > secondary > tertiary. This is the order in which the proton donor character of the alcohols lies [8]. However, if the quenching effect of the alcohols were due to their high viscosity then the quenching constants should follow the order tertiary > sec-

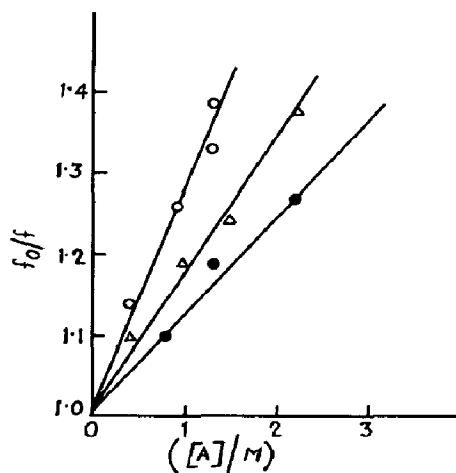


Fig. 3. Quenching of excimer emission from the  $2 \times 10^{-4}$  pyrene-0.6 M DMA system in n-heptane with n-butyl alcohol ( $\circ$ ), sec-butyl alcohol ( $\Delta$ ) and tert-butyl alcohol ( $\bullet$ ).

**TABLE 2**  
**Quenching constants for various alcohols**

Solvent	Pyrene-DMA	Anthracene-DMA
n-Butyl alcohol	1.29	1.28
sec-Butyl alcohol	1.18	1.16
tert-Butyl alcohol	1.12	1.10

ondary > primary, *i.e.* the order in which their viscosity increases. This is contrary to experimental findings.

It appears therefore that the solvent effect is quite a complicated phenomenon in which both specific and non-specific interactions participate; hence no simple mechanism for the effect of solvents on exciplex emission can be proposed.

### References

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