

Short Communication

The formation of intramolecular exciplexes by derivatives of 1-methylnaphthalene

G. S. BEDDARD and R. S. DAVIDSON*

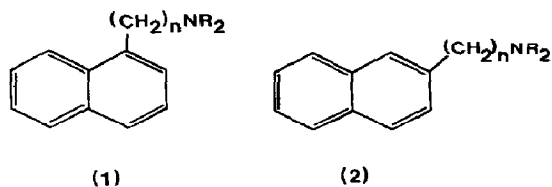
The Davy Faraday Research Laboratory, The Royal Institution, 21, Albemarle Street, London, W.1. (Gt. Britain)

and A. LEWIS

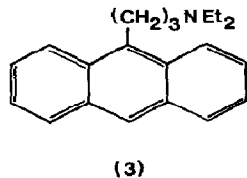
Department of Chemistry, The University, Leicester LE1 7RH (Gt. Britain)

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Naphthylalkylamines^{1,2} of the type (1) and (2)

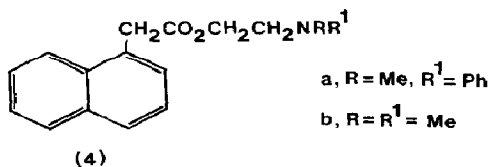


and anthrylalkylamines^{2,3} of the type (3)



have been recently reported to exhibit intramolecular exciplex formation^{1,2}. It was found that for compounds (1) and (2), intramolecular exciplex formation did not take place when $n > 3$ ¹.

We wish to report⁴ that compounds of the type (4) exhibit intramolecular exciplex formation although there are more than three linking carbon atoms between the amino group and the naphthalene residue. The ultra-violet absorption spectra of (4a) and (4b)



* Reprint requests should be addressed to the author's present address: Department of Chemistry, The University, Leicester LE1 7RH (Gt. Britain).

showed there to be no interaction between the amino groups and the naphthalene nucleus and the emission spectra were independent of the concentration (in the range $10^{-2} M$ – $10^{-5} M$). In the case of (4a) increasing the polarity of the solvent leads to a red shift in the wavelength of maximum intensity for emission of the exciplex band (see Fig. 1) with a concomitant decrease in intensity. Only in the case of (4b) did a change of solvent from cyclohexane to acetonitrile cause the complete quenching of exciplex fluorescence.

Experimental

The fluorescence decay curves were measured by the single photon counting technique⁵. The excitation source was a 4 ns half-width light pulse from a free running spark lamp operating at 8 kHz in an oxygen atmosphere. The wavelength of the exciting light was chosen by a Bausch and Lomb Monochromator type 33-86-02, using a 0.5 nm bandpass. Emission was observed through wide band filters (30 nm wide for an optical density of 2) centred at 340 nm and 400 or 490 nm for the monomer and exciplex emissions respectively. The fluorescence was detected by a water-cooled ($\sim 15^\circ\text{C}$) E.M.I. 9813 KB photomultiplier.

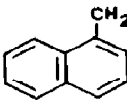
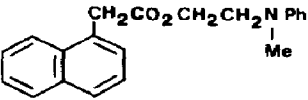
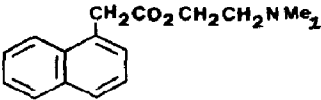
When the lifetime was observed to be short (< 10 ns), convolution analysis was performed to determine the lifetime of the fluorescence. Spectra were recorded with a Hitachi-Perkin-Elmer Fluorimeter (HTV R213 photomultiplier tube).

Results and discussion

We have previously observed exciplex emission from (1), $n = 2$ or 3, $R = \text{Et}$, when dissolved in highly polar solvents such as acetonitrile². In contrast, intermolecular exciplexes of aromatic hydrocarbons and amines do not fluoresce in such solvents⁶⁻⁹.

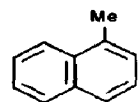
In order to understand the effect of solvent upon intramolecular exciplex formation, we studied the lifetimes of the emission of exciplexes and the methyl-naphthalene moiety in compounds (1), $n = 2$, $R = \text{Et}$, and (4a) and (4b). Measurements were made for both air-saturated and degassed solutions, and these are shown in Table 1. These results show that the decay times of the exciplex are increased as a result of change of solvent from cyclohexane to acetonitrile, *i.e.* the exciplexes are more stable in polar solvents. This contrasts with the previous finding that the decay time of intermolecular exciplexes is shortened by a change from a non-polar to a polar solvent^{8,9}. Oxygen quenches the emission from both the 1-methylnaphthalene residue and the exciplex. Small time delays (~ 3 ns) in the build-up of the exciplex were observed for compounds (1), $n = 2$, $R = \text{Et}$, and (4b). With compound (4a), time delays of 9 ns and 12 ns were observed for the build-up of exciplex in degassed cyclohexane and acetonitrile solutions respectively. The decay of the exciplex emission was found to be nearly exponential with respect to time. In all cases measurements were made for compounds excited at 298 nm. At this wavelength the amino group as well as the naphthalene nucleus absorb.

TABLE 1
LIFETIMES (ns) OF THE FLUORESCENCE EXHIBITED BY SOME NAPHTHYLALKYLAMINES ($10^{-4}M$)

Compound	Solvent				
	Cyclohexane		Acetonitrile		
	Monomer	Exciplex	Monomer	Exciplex	
	A	M	11.7*	9.2	6.4
	An	M	13.6*	57.5	~ 30
	A	M	10*	1.5	12.5
	An	M	32	50.5	61.5*
	A	10.6*	11	1.6	N.O.
	An	28	28	57	N.O.

A = Air saturated solutions; An = de-oxygenated solutions; M = Masked by exciplex emission
N.O. = No emission observable.

* Indicates exponential decay.

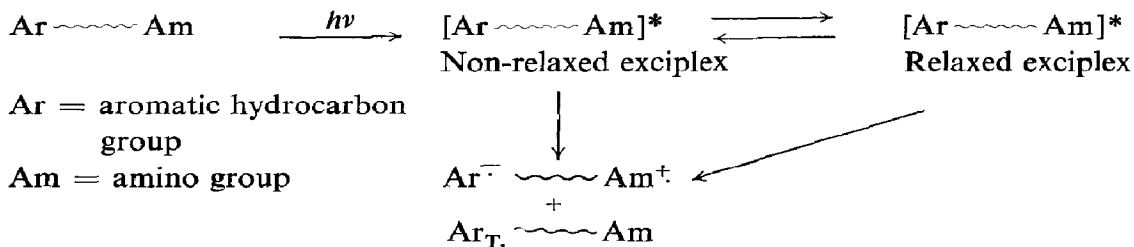


$$\begin{aligned}\tau_F &= 83 \text{ ns (cyclohexane An)} \\ &= 14.8 \text{ ns (cyclohexane A)}\end{aligned}$$

The extent to which exciplex formation takes place as a result of exciting the amino group as opposed to the naphthalene nucleus will drastically affect the time delay¹⁰. The shorter time delays observed when a dialkylamino group is present, compared with when an arylamino group is present, is no doubt due to exciplex formation resulting from excitation of the amino group. The longer lifetime of the arylamino group allows more time for exciplex formation and consequently longer time delays are observed with this group. Under conditions in which exciplex formation takes place from excitation of the naphthalene nucleus, relatively long time delays in build-up of exciplex are observed^{10,11}. The non-exponential decays observed for some compounds indicate that "fluorescent" exciplex formation is a reversible process¹².

It has recently been proposed that exciplex formation between aromatic hydrocarbons and amines initially involves the formation of a non-fluorescent exciplex¹³⁻¹⁶. This has been termed a non-relaxed exciplex. Reorientation of the solvent around this exciplex leads to a relaxed exciplex which is capable of fluorescing¹⁵. Also, the non-relaxed exciplex may either dissociate into radical ions or decay giving the triplet hydrocarbon^{14,16}.

With the intramolecular exciplexes (1), $n = 2$, $R = Et$, and (4a), the interesting situation arises that although their quantum yields of exciplex fluorescence are lower in acetonitrile than in cyclohexane (see Fig. 1) the lifetimes of the exciplexes are greater in the more polar solvent. This dichotomy can be understood if an intermediate non-relaxed exciplex is postulated:



Apparently with compound (1), $n = 2$, $R = Et$, and with (4a) complete dissociation of the non-relaxed exciplex does not occur in acetonitrile solution. The greater lifetimes of the relaxed exciplexes in this solvent than in cyclohexane reflects the greater solvating power of acetonitrile and also demonstrates that dissociation of the relaxed exciplex into radical ions is not an important process. Acknowledgement of this latter fact allows one to say that the decrease in quantum yield of exciplex fluorescence as the polarity of the solvent is increased is due to dissociation of the non-relaxed exciplex occurring to a greater extent in the more polar solvent. Dissociation of the non-relaxed exciplex of (4b) apparently occurs

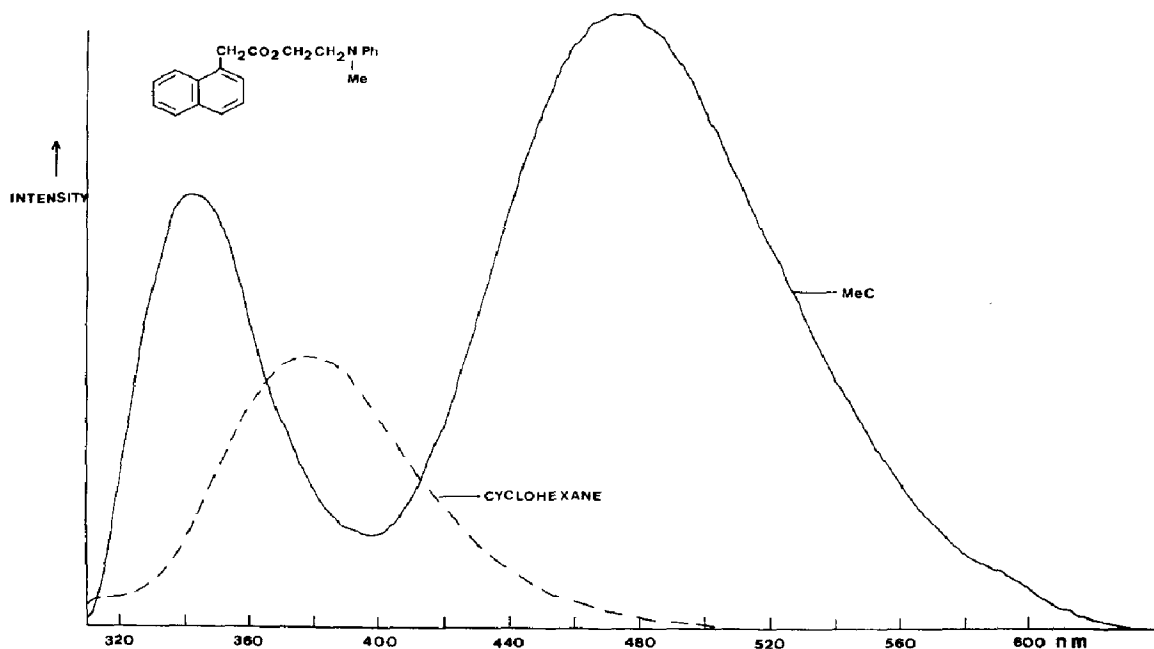


Fig. 1. Fluorescence emission recorded for (4a) in cyclohexane and acetonitrile solution. (Intensity scale for cyclohexane ~ 30 times that for acetonitrile solution.)

extremely efficiently in acetonitrile solution since no exciplex emission was observed in this solvent.

Another point of interest is that compounds (4a) and (4b) exhibit exciplex emission even though there are more than three carbon atoms linking the amino group to the aromatic hydrocarbon. Molecular models show that the ester group allows the methylene units to adopt a staggered conformation when the amino group is situated over C₁ or C₂ of the naphthalene nucleus. Thus an important criterion for the observation of intramolecular exciplex formation appears to be that the linking units should be able to adopt a conformation in the exciplex in which there is a minimum of non-bonded interactions.

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