

PHOTOPHYSICS OF SIMPLE SATURATED AMINES

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Simple tertiary aliphatic amines have been known to be strongly fluorescent for some time¹, but the excitation energy dependence of this emission has not hitherto been investigated. In table 1 we present some quantum yield data for isolated (0.1 torr) triethylamine (TEA) obtained from fluorescence excitation spectroscopy, and fluorescence decay times. The latter are seen to become distinctly non-exponential at short wavelengths of excitation (Figure 1). Possible reasons for this will be discussed.

Table 1

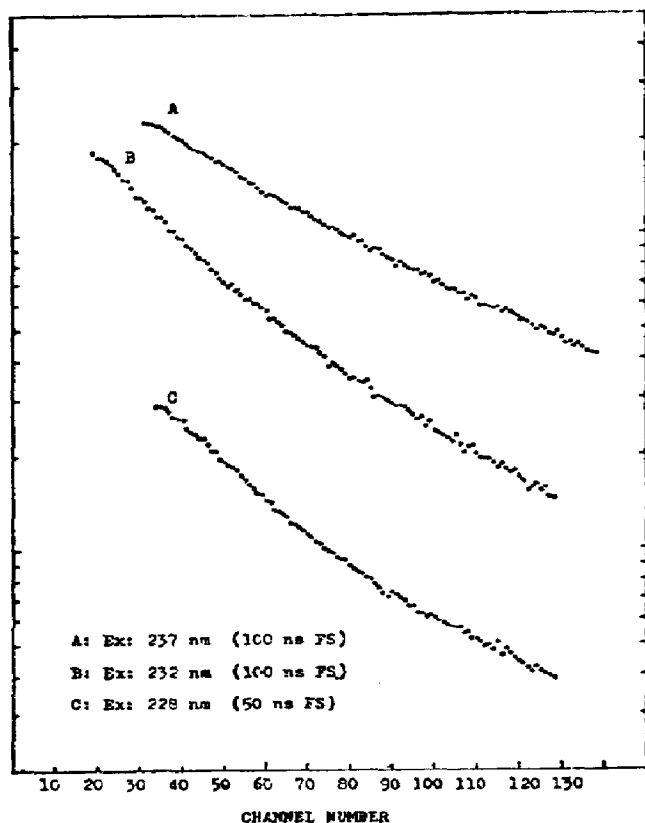
Fluorescence quantum yields and decay times of TEA, 0.1 torr

λ_{ex} /nm	ϕ_F	$(\phi_F)R^a$	τ_F^b /ns	τ_S^c /ns	τ_L^c /ns	$(\tau_F)R^{a,b}$ /ns
260	1.0		55	-	-	-
250	1.0		55	-	-	55
240	0.77	0.93	-	46	47	54
235	0.48	0.88	-	28	41	52
230	0.21	0.78	-	14	17	52
220	0.03	0.47	-	5	12	55
215	0.01	0.25	-	-	-	-

a Values in presence of 60 torr cyclohexane

b Single exponential decay observed

c Non-exponential decay observed, with components of approximate magnitude indicated.



Fluorescence decays of
0.1 torr TEA

The vibrationally relaxed excited singlet state of TEA (and other aliphatic amines) has been shown to be strongly quenched in solution and gas phase by simple fluorocarbons and chlorocarbons. Thus the bimolecular rate constant for quenching of singlet TEA by perfluoromethylcyclohexane is $2.5 \pm 0.2 \times 10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ in the gas phase, $1.3 \pm 0.2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ in cyclohexane solution. Such efficient quenching by fluorocarbons is unusual, and although ground-state interactions cannot be ignored, it is likely that non-fluorescent exciplex formation involving transfer of charge from excited amine to halocarbon is the quenching mechanism.

Related fluorescent exciplexes in which these amines act as unexcited donors to singlet electronically excited 9-cyano-anthracene have been

observed in the vapour phase at elevated temperatures. (Figure 2). From an analysis of the kinetics of the exciplex emission and a comparison with solution-phase data it will be shown that the rate-constant for radiative decay of the exciplex must be very much larger in the vapour phase than the value in even non-polar solution.

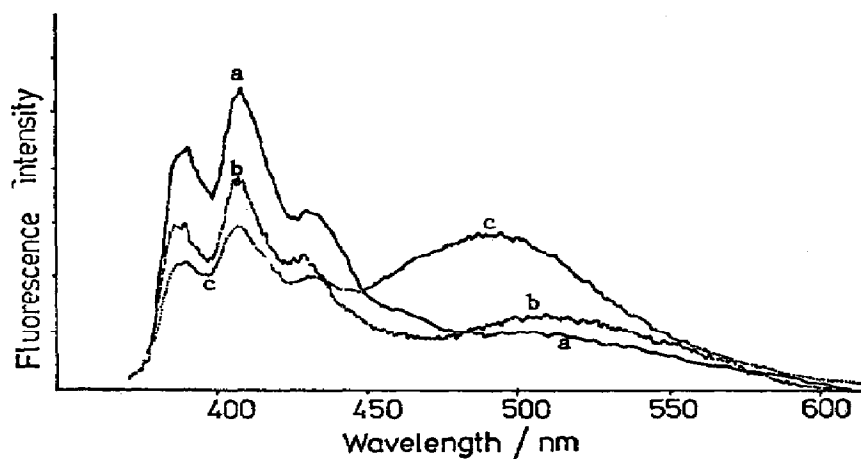


Figure 2 Vapour-phase fluorescent 9-CN-A-aliphatic amine exciplexes

- a 9-CN-A-triethylamine, 185°C
- b 9-CN-A-tributylamine, 231°C
- c 9-CN-A-dimethylaniline, 231°C

References

1. A.M. Halpern, Mol. Photochem. 5, (1973), 517.