The Photophysics of Some Tertiary Aliphatic Amines in Solution

Richard A. Beecroft and R. Stephen Davidson *
Department of Chemistry, The City University, Northampton Square, London EC1V 0HB

The absorption and fluorescence properties of some *N*-methyl alicyclic amines are reported. Absorption maxima, fluorescence emission wavelength maxima, and fluorescence lifetimes are highly dependent upon amine structure. The Stokes shift is also dependent upon amine structure and this is suggested as being a reflection of the extent to which the amino group is pyramidal in the ground state. In many cases, change of solvent from cyclohexane to tetrahydrofuran causes a large red shift in wavelength for maximum fluorescence intensity, but often has little effect upon fluorescence lifetime, which indicates that solvent effects upon non-radiative processes occur largely before the solvated planar state of the amine is created. Examples of the quenching of amine fluorescence by hydroxy groups and of excited amines forming exciplexes with benzene are presented.

The photophysics of acyclic tertiary amines has been thoroughly investigated by Halpern and co-workers.[1-4] Tertiary amines exhibit fluorescence both in the gas phase[2] and in non-polar solvents such as n-hexane and cyclohexane.[3,4] In cyclohexane solution the emission is usually broad and structureless. This, together with the finding that the amines possessing flexible structures exhibit large Stokes shifts, is in accord with the view, that by analogy with ammonia,[5] the initially created excited amine molecule undergoes relaxation to give a planar species from which emission occurs. This view is also backed up by the finding that the fluorescence intensity of these amines is temperature dependent.[4]

The nature of the emitting state in solution is a matter of some debate. Muto *et al.*[6] and later Halpern[1] showed that many tertiary amines fluoresce in polar solvents such as tetrahydrofuran. The emission is substantially red shifted from that observed in cyclohexane solution. The current view is that these solvatochromic shifts are due to the emission emanating from a Rydberg state, which can be solvated by ion–dipole interactions. Such a model is reminiscent of that used to explain solvent effects upon exciplex emission.[7] When solvents more polar than tetrahydrofuran are employed, the amine fluorescence is quenched.[8]

Another particularly interesting feature of amine photophysics is the ability of some tertiary amines to form excimers.[2,3] The structure and bonding characteristics of these amines is a matter of some debate. Many amines, *e.g.*, triethylamine, which do not exhibit fluorescent excimer formation exhibit concentration quenching.

We now report some photophysical studies upon alicyclic amines in which the ring size is varied and also upon the way in which solvent affects these properties.

Results

Figure 1 shows the absorption spectra for a series of amines at a concentration of 10^{-2}M in cyclohexane solution. It can be seen from the Figure and from Table 1 that the molar extinction coefficients for the amines at a particular wavelength and the wavelength of the absorbance band edge are dependent upon the amine structure.

The quantum yields of fluorescence for the amines in degassed cyclohexane solution were determined at three wavelengths (240, 250, and 265 nm), in order to observe whether the quantum yields were concentration dependent. Fluorescence lifetimes were determined at these wavelengths using the technique of pulse-sampling fluorimetry (Table 2). By combining the data from Tables 1 and 2, a crude estimate of the self-quenching rate constants (Table 3) was obtained. In most cases the values were close to the diffusion-controlled limit.

The amines exhibit fluorescence in tetrahydrofuran solution and the quantum yields and fluorescence lifetimes are shown in Table 4. In all cases, the fluorescence spectra recorded for amines in tetrahydrofuran solution lacked any well resolved features. In a few cases, it was noted that the spectral distribution of the fluorescence exhibited a small dependency upon oxygen concentration which suggested that, in oxygenated solution, emission from amine–oxygen complexes may be being observed. When solvents more polar than tetrahydrofuran were used, *e.g.*, acetonitrile and ethanol, fluorescence could not be observed. The ability of the hydroxy group to quench fluorescence is shown particularly well by aminoalcohols (Table 5). In cyclohexane solution, the hydroxy group of the ω-aminoundecanol has little effect whereas with the ethanolamines, the hydroxy groups led to almost total fluorescence quenching. The presence of the hydroxy groups in all the amines studied attenuates the fluorescence intensity in tetrahydrofuran solution.

Although it is difficult to describe accurately the solvating ability of benzene, one knows from exciplex chemistry,[7] that its ability to solvate excited complexes is less than that of tetrahydrofuran. However, the fluorescence observed when the amines are excited in benzene solution (Table 6) is red shifted from that observed in tetrahydofuran solution. This observation, together with the results from our earlier work on benzene–amine exciplexes,[9,10] leads us to propose that the emissions observed in benzene solution emanate from benzene-solvated benzene–amine exciplexes.

Discussion

From the absorption and emission spectra of the amines it is possible to derive the Stokes shifts for the amines (Table 6). The largest shift is that for the *N,N'*-dimethylpiperazine. Other amines, *e.g.*, *N*-methylpiperidine, which have the nitrogen atom in a six-membered ring also display relatively large Stokes shifts as do triethylamine and *N*-methylpyrrolidine. As the size of the ring is increased above six so the Stokes shifts decrease suggesting that ring size influences the extent to which the amino group has a pyramidal structure. The less pyramidal the nitrogen atom in the ground state, the less configurational reorganisation will occur after excitation and consequently the smaller the Stokes shift. For amines in which the nitrogen is pyramidal and cannot become planar because of its environment, Stokes shifts are not observed.[3b] For all the amines studied, concentration quenching (Table 3) but no excimeric emission was observed. This perhaps is not surprising when one

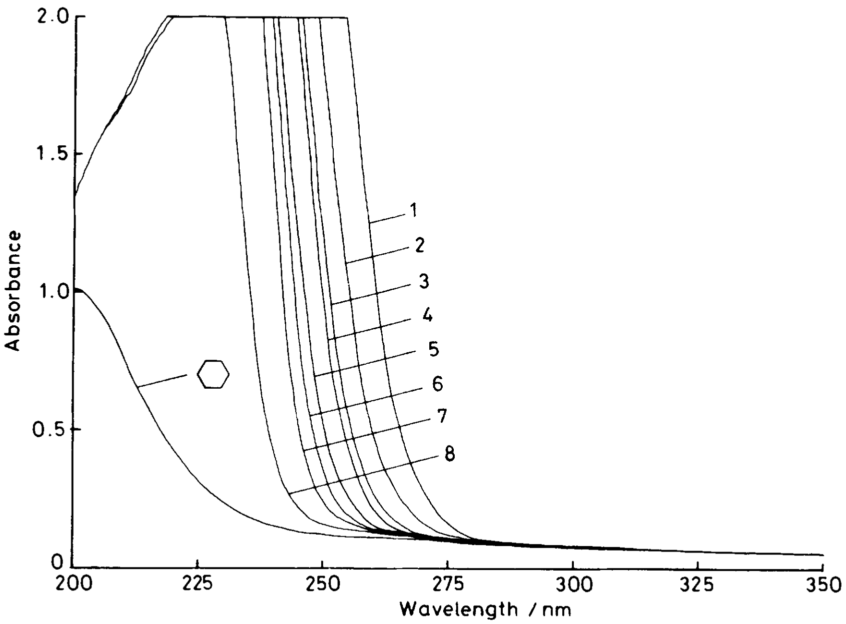
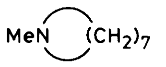
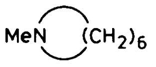
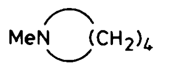


Figure 1. U.v. absorption spectra of aerated cyclohexane solutions of tertiary alicyclic and acyclic saturated amines (1.0×10^{-2} mol dm^{-3}) recorded at 20 °C

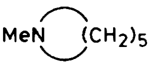
(**1**)


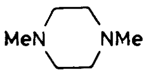
(**2**)


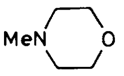
(**3**)


(**4**) NEt_3

(**5**) $MeNEt_2$

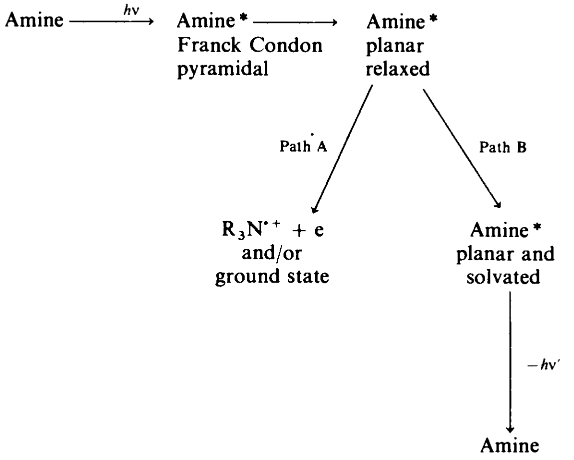
(**6**)


(**7**)


(**8**)


considers that all the amines are conformationally mobile and, consequently, the energy of a collision complex can be readily dissipated non-radiatively by inducing conformational changes.[11] A similar situation was observed for excited complexes formed between 1,1′-binaphthyl and pyrroles.[11]

All the amines exhibited fluorescence in tetrahydrofuran solution which was red shifted from that found in cyclohexane solution. As can be seen from the Tables, the change to a more polar solvent usually caused a decrease in quantum yield of fluorescence and in some cases the change caused an increase in lifetimes. This result is not without precedent,[1] but is difficult to explain. One either has to assume that for some amines the radiative decay rate constant (k_f) varies with solvent or else invoke the intervention of a non-emitting excited state, which can relax to give the fluorescent state and/or give rise to non-radiative processes, as shown in the Scheme. The relative efficiencies of paths A and B will determine the quantum yields of fluorescence but provided that path B is irreversible, the lifetime will be governed by the radiative properties of the solvated amine, the solvent possibly playing an important part. It is interesting to note that the differences between the Stokes shifts in cyclohexane and tetrahydrofuran solutions are very similar for all the amines (see Table 6). This suggests that the solvation by tetrahydrofuran of each of the amines is very similar.



Scheme.

Polar solvents also markedly affect the efficiency of the non-radiative decay routes for the excited amine, a situation very similar to that found for excited charge-transfer complexes. Excited amines are known to undergo electron ejection in

Table 1. Molar extinction coefficients (ε) of a series of tertiary alicyclic amines and selected acyclic amines in aerated cyclohexane solution at wavelengths of 240, 250, and 265 nm. The effective concentration of the amine at each wavelength is shown in parentheses

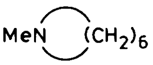
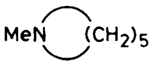
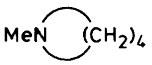
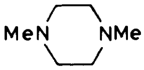
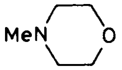
Amine	ε/mol^{-1} dm^3 cm^{-1} 240 nm	250 nm	265 nm	Absorbance band edge (cm^{-1} × 10^4)
	1 025 (9.7 × 10^{-5})	360 (2.7 × 10^{-4})	42 (2.3 × 10^{-3})	3.57
	520 (1.9 × 10^{-4})	165 (6.0 × 10^{-4})	13 (7.6 × 10^{-3})	3.60
	160 (6.2 × 10^{-4})	24 (4.2 × 10^{-3})	4 (2.5 × 10^{-2})	3.88
	350 (2.8 × 10^{-4})	88 (1.1 × 10^{-3})	5.5 (1.8 × 10^{-2})	3.70
NEt_3	400 (2.5 × 10^{-4})	84 (1.2 × 10^{-3})	3 (3.3 × 10^{-2})	3.78
$MeNEt_2$	171 (5.8 × 10^{-4})	32 (3.1 × 10^{-3})	2 (5.0 × 10^{-2})	
	120 (8.3 × 10^{-4})	13 (7.7 × 10^{-3})	2 (5.0 × 10^{-2})	3.88
	28 (3.6 × 10^{-3})	4 (2.5 × 10^{-2})	1.5 (6.7 × 10^{-2})	3.88

Table 2. Quantum yields of fluorescence (relative to toluene φ_f = 0.14) and fluorescence lifetimes (ns) of a series of alicyclic tertiary amines in degassed cyclohexane solution at the excitation wavelengths shown

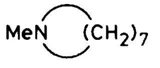
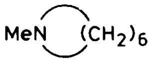
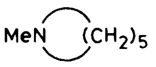
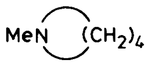
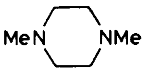
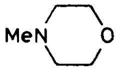
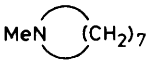
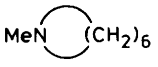
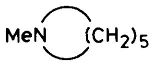
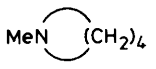
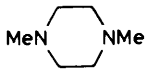
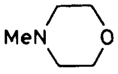
Amine	$\lambda_{exc.}$ 240 nm φ_f	τ_f/ns	$\lambda_{exc.}$ 250 nm φ_f	τ_f/ns	$\lambda_{exc.}$ 265 nm φ_f	τ_f/ns
	0.52	34	0.63	36	0.44	32
	0.50	35	0.55	38	0.19	30
	0.29	32	0.22	41	(0.01)	18
	0.50	31	0.48	34	0.13	24
NEt_3	0.44	37	0.44	54	0.27	32
	0.48	116	0.23	110		105
	0.32	36	0.04	24	0.01	

Table 3. Estimated self-quenching rate constants for a series of alicyclic tertiary amines in degassed cyclohexane solution, based upon data from Tables 1 and 2

Amine	Self-quenching rate constant (dm^3 mol^{-1} s^{-1})
	5.36 × 10^9
	6.55 × 10^9
	
	4.65 × 10^9
NEt_3	3.54 × 10^8
	1.3 × 10^9
	7.78 × 10^9

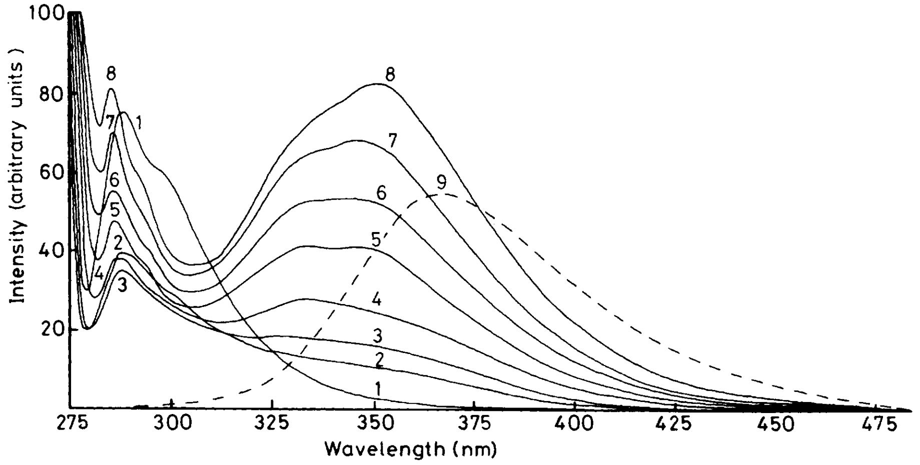


Figure 2. Fluorescence spectra of aerated cyclohexane solutions of $\mathrm{MeN(CH_2)_6}$ (absorbance 0.1 at 275 nm) + benzene (μl): (1) 0.0M; (2) 10 μl, 3.75 × 10^{-2}M; (3) 20 μl, 7.5 × 10^{-2}M; (4) 40 μl, 1.5 × 10^{-1}M; (5) 80 μl, 3.0 × 10^{-1}M; (6) 125 μl, 4.69 × 10^{-1}M; (7) 200 μl, 7.5 × 10^{-1}M; (8) 500 μl, 1.88M; (9) $\mathrm{MeN(CH_2)_6}$ in benzene (absorbance 0.1 at 290 nm)

Table 4. Quantum yields of fluorescence (relative to toluene $\varphi_f = 0.14$) and fluorescence lifetimes (ns) of a series of tertiary alicyclic amines in degassed tetrahydrofuran solution at an excitation wavelength of 250 nm

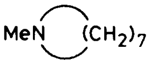
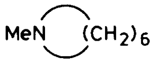
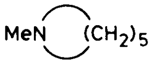
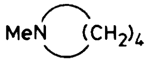
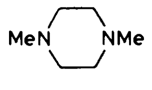
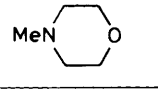
Amine	φ_f	τ_f/ns
	0.34	43
	0.31	46
	0.15	37
	0.29	35
NEt3	0.30	53
	0.09	39
	0.07	36

Table 5. Fluorescence maxima (nm) and quantum yields of fluorescence (relative to toluene $\varphi_f = 0.14$) for selected aminoalcohols in degassed cyclohexane and tetrahydrofuran solutions at 20 °C

	Cyclohexane		THF	
Amine	$\lambda_{max.}$/nm	φ_f	$\lambda_{max.}$/nm	φ_f
NEt_3	285	0.44	335	0.30
$Et_2N(CH_2)_{11}OH$	287	0.31	335	0.05
$Me_2NCH_2CH_2OH$	294	0.01	357	0.06
$MeN(CH_2CH_2OH)_2$	290	<0.01	360	0.05
$N(CH_2CH_2OH)_3$	290	<0.01	363	0.02

highly polar solvents and this process is akin to that of the formation of radical ions from exciplexes. Alcohols are effective quenchers of exciplex and amine fluorescence.[12] This was observed for the ethanolamines in cyclohexane solution. The situation is somewhat alleviated in tetrahydrofuran solution where the hydroxy groups hydrogen bond to the solvent. The presence of the hydroxy groups also causes a red shift in the fluorescence of the amines, suggesting that they play a part in the solvation of the excited amine. From the conditions employed it is impossible to assess the extent to which this is intermolecular. The most difficult result to explain is that for the aminoundecanol, where the quantum yield of fluorescence plummets on change of solvent from cyclohexane to tetrahydrofuran. In this compound, the hydroxy group is sufficiently remote from the amino group for there to be an insignificant intramolecular interaction and therefore the lack of an effect in cyclohexane solution is not surprising. The quantum yields of fluorescence in tetrahydrofuran solution similar to those for the ethanolamines, suggesting that the solvent favours some solvation or protonation of the excited amine.

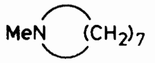
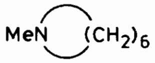
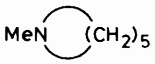
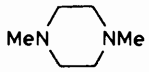
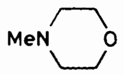
From Figure 2 one can see the profound influence that benzene solvation has upon benzene–amine exciplexes and that when high benzene concentrations are employed, the emission resembles that of a benzene-solvated benzene–amine exciplex. Since care was taken to ensure that most of the exciting light was absorbed by the amine, by utilising an excitation wavelength of 275 nm, we propose that the excited amines form an exciplex with benzene, which then undergoes solvation. The very low molar extinction coefficients of some amines at 275 nm prevented us examining all the amine systems.

Experimental

Solvents used for the absorption and fluorescence spectroscopy were as follows: cyclohexane (Hopkin and Williams Spectrosol grade), benzene (Merck, Uvasol grade), and tetrahydrofuran (BDH Chemicals). The latter was distilled from lithium aluminium hydride prior to use. The amines (Aldrich) were distilled and purified by preparative gas–liquid chromatography (Pye Unicam 105, 20% Peg A column) prior to use.

U.v.–visible absorption spectra were recorded using a Perkin-Elmer 402 spectrometer and fluorescence spectra measured with

Table 6. Fluorescence wavelength maxima (nm) of selected tertiary alicyclic amines and triethylamine in degassed solutions of cyclohexane, benzene, and tetrahydrofuran together with Stokes shift values in cyclohexane and tetrahydrofuran solution

		λ_{max}/nm		Stokes shift ($\times 10^3$ cm^{-1})		
Amine	Cyclohexane	Benzene	THF	Cyclohexane	THF	Cyclohexane–THF
	287	365	340	0.9	6.3	5.4
	289	363	345	1.4	7.0	5.6
	295	384	355	4.9	10.6	5.7
	295	367	345	3.1	8.0	4.9
NEt$_3$	285	360	335	2.7	7.95	5.25
	316		380	7.2	13.5	6.3
	280		340	3.1	9.4	6.3

an uncorrected Perkin-Elmer MPF-4 fluorescence spectrometer. The fluorescence spectra of the solvent blanks were run in each case, to check that they showed negligible emission at maximum sensitivity over the wavelength range monitored for the amine emission experiments. For recording the amine emission spectra, solutions of the amines were made up in 1 cm path-length quartz rectangular fluorimeter cells to an absorbance of 0.1 at the excitation wavelengths (240, 250, and 265 nm). The solutions were degassed *via* several freeze–pump–thaw cycles. Quantum yields of fluorescence were determined relative to toluene ($\varphi_f = 0.14$).[13]

Fluorescence lifetimes were determined using the pulse-sampling method.[14] Excitation was provided by the discharge from a free running nanosecond flash lamp (Applied Photophysics model 311) giving repetition rates up to *ca.* 10 KHz (depending upon the applied voltage, gas pressure, and electrode gap), with a discharge duration of 1–2 ns. The light was passed through a Bausch and Lomb monochromator before falling on the sample and the emission was detected by an EMI Type 9813 KB photomultiplier tube. The output of the multiplier tube together with that from a trigger photomultiplier tube (EMI 931A tube) were fed to a Bradley Electronics Sampling Adaptor Type 158, the output of which was displayed on a *X–Y* recorder (Advance, HR-100). Decays were digitised by hand and the reported lifetimes are the average of ten separate measurements.

Acknowledgements

We thank the S.E.R.C. for a maintenance awared (to R. A. B) and the Royal Society for funds to purchase the fluorescence lifetime apparatus.

References

1 A. M. Halpern, *J. Phys. Chem.*, 1981, **85**, 1682.
2 A. M. Halpern, J. L. Roebber, and K. Weiss, *J. Chem. Phys.*, 1968, **49**, 1348; A. M. Halpern, *Chem. Phys. Lett.*, 1970, **6**, 296; A. M. Halpern, *J. Am. Chem. Soc.*, 1974, **96**, 4392, 7655; A. M. Halpern and P. P. Chan, *ibid.*, 1975, **97**, 2971; C. G. Cureton, K. Hara, D. V. O'Connor, and D. Phillips, *Chem. Phys. Lett.*, 1980, **73**, 231; Y. Matsumi and K. Obi, *Chem. Phys.*, 1980, **49**, 87; K. Obi and Y. Matsumi, *ibid.*, p. 95.
3 (*a*) A. M. Halpern and R. M. Danziger, *Chem. Phys. Lett.*, 1972, **16**, 72; A. M. Halpern and E. Maratos, *J. Am. Chem. Soc.*, 1972, **94**, 8273; A. M. Halpern and T. Gartman, *ibid.*, 1974, **96**, 1393; (*b*) A. M. Halpern, P. Ravinet, and R. J. Sternfels, *J. Am. Chem. Soc.*, 1977, **99**, 169; (*c*) A. M. Halpern, B. R. Ramachandran, and S. Sharma, *J. Phys. Chem.*, 1982, **86**, 2049.
4 A. M. Halpern and D. K. Wong, *Chem. Phys. Lett.*, 1976, **37**, 416.
5 A. D. Walsh and P. A. Warsop, *Trans. Faraday Soc.*, 1961, **57**, 345; A. E. Douglas, *Faraday Discuss. Chem. Soc.*, 1963, **35**, 158.
6 Y. Muto, Y. Nakato, and H. Tsubomura, *Chem. Phys. Lett.*, 1971, **9**, 597.
7 R. S. Davidson, *Adv. Phys. Org. Chem.*, 1983, **19**, 1 and references cited therein.
8 A. M. Halpern and K. Wryzykowska, *J. Photochem.*, 1981, **15**, 147.
9 R. A. Beecroft and R. S. Davidson, *Chem. Phys. Lett.*, 1981, **77**, 77.
10 H. Leismann and J. Mattay, *Tetrahedron Lett.*, 1978, 265.
11 X.-J. Luo, G. S. Beddard, G. Porter, and R. S. Davidson, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3477.
12 D. R. G. Brimage and R. S. Davidson, *J. Photochem.*, 1972/73, **1**, 79.
13 I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965.
14 W. R. Ware, in 'Creation and Detection of Excited States,' ed. A. A. Lamola, Marcel Dekker, New York, 1971, vol. 1A.

Received 1*st October* 1984; *Paper* 4/1685